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SCHOOL OF CHEMICAL SCIENCES
and
SCHOOL OF LIFE SCIENCES

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CHEMISTRY AND BIOLOGY OF TRACE METALS IN THE ENVIRONMENT

Sponsored in cooperation with the
ILLINOIS INSTITUTE FOR ENVIRONMENTAL QUALITY
and
THE ENVIRONMENTAL STUDIES PROGRAM, GRADUATE COLLEGE,

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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SCHOOL OF CHEMICAL SCIENCES
and
SCHOOL OF LIFE SCIENCES

Seminar Series - Spring, 1971

CHEMISTRY AND BIOLOGY OF TRACE METALS IN THE ENVIRONMENT

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UNIVERSITY OF ILLINOIS

URBANA, ILLINOIS

FOREWORD

A seminar series "Chemistry and Biology of Trace Metals in the Environment" was sponsored jointly by the School of Chemical Sciences and the School of Life Sciences of the College of Liberal Arts and Sciences, University of Illinois at Urbana-Champaign, during the Spring semester of 1971. It was offered as a course listed as Chemistry 199 and 490, and Biology 199 and 490, open to undergraduate and graduate students from any college of the university.

At that time, a Metals Task group was in Phase I, Exploratory and Planning Phase, of a research project, Environmental Effects of Pollution by Lead and Other Metals, under the IRRPOS program of the National Science Foundation. Several of the speakers were participants in that research effort, and are continuing as members of Phase II of the project, now supported by the RANN program of the National Science Foundation, and under the Environmental Studies Program of the University of Illinois.

A grant to defray the expenses of some of the visiting speakers and the costs of publication was received from the Illinois Institute for Environmental Quality. This support is gratefully acknowledged.

H. A. Laitinen, Professor of Chemistry

R. L. Metcalf, Professor of Zoology
and Entomology

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SEMINAR SERIES

CHEMISTRY AND BIOLOGY OF TRACE METALS IN THE ENVIRONMENT

Spring - 1971, University of Illinois
Urbana-Champaign Campus

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CHEMISTRY OF TRACE METALS IN THE ENVIRONMENT

H. A. Laitinen

First, I would like to make a few preliminary announcements about the Seminar Series itself. It is sponsored jointly by the School of Chemical Sciences and the School of Life Sciences. In addition, we are getting some aid from the Illinois Institute for Environmental Quality, which is defraying the cost of some visiting speakers and the preparation of a final written version of these talks.

I'd like to dwell a little on the content of the lecture series before we get into today's talk specifically. Essentially, this is an interdisciplinary seminar series which is going to cover a wide variety of approaches to the general problem of trace metals in the environment. You might ask, Why do we limit it to trace metals? Why not have a seminar series on pollution? Essentially there are two reasons for this. In the first place it allows us to restrict the topic somewhat to make it amenable to a treatment of this length. And in the second place, here at the University of Illinois we have an interdisciplinary project now going on which is centered around the environmental consequences of pollution by lead. This has been going on actively for the last year or so and in the planning stage longer than that. But in the future it is expected that this project will expand to include a number of the other trace metals. It is particularly fitting, then, that we have some of our own experts from various disciplines, for example the agriculture college, the engineering college, and the State Surveys here on campus as well as chemistry and biology.

The first thing I would like to dwell upon is the scope of the environment itself. We can speak of five principal elements: the air, the water, the land, the animal kingdom, and the plant kingdom. You might ask why animals and plants are included in the environment. Of course they do constitute the environment for whatever species might be living on them or in them. For instance, the bacteria in your digestive system might be at this moment having a little conference on what to do about the garbage in the form of antibiotics or things of that type that this human is ingesting. It is a comprehensive subject, and of these the plant and animal kingdoms are in the realm of biology. Professor Metcalf will give a very general talk on this topic and I will try not to infringe on his subject. So today we are going to be concerned principally with metals in the three other aspects: the air, the water and the land, as they relate to environmental pollution. The way that I propose to do this is not by taking a serious look at all of the metals you can think of, but rather, by trying to examine certain chemical principles and generalizations that we might bring to bear on this problem and thereby perhaps approach it a little more intelligently.

The first point I would like to start with is the finite magnitude of the environment, the finite scope. The way we shall start this is by putting our attention on the atmosphere, in asking a rather silly-sounding question. The question is this: Suppose that Julius Caesar, when he expired, emitted a certain number of nitrogen atoms into the atmosphere from the air in his lungs, and after all the mixing during the last 2000 years now you and I are to breathe our next lungfull, what is the probability that we are going to pull in one or more of these nitrogen atoms that he exhaled? How could we approach this problem?

First of all we must estimate the total magnitude of the atmosphere. We can readily calculate that the area of the earth is $5x10^{18}$ cm^2, and from the barometric pressure that each cm^2 supports about 10^3 g of atmosphere. Knowing the average molecular weight of air (29), and Avogadro's number ($6x10^{23}$) we come out with 10^{44} molecules. When Mr. Caesar expired, let us say he exhaled 1 liter of air, which is 1/20 of a mole or $3x10^{22}$ molecules. So we might estimate the probability of picking one molecule from the atmosphere and finding one that had come from Mr. Caesar as $3x10^{-22}$. We have to be careful because the nitrogen atoms scramble among the molecules, but the original question was phrased in terms of atoms, which are inviolate, and what is more practically all of the nitrogen atoms in the world at any time are in the atmosphere. There is a negligible part in the biosphere. Now in your next breath you are going to pick, not one, but say $3x10^{22}$ atoms. So we multiply $3x10^{-22}$ by $3x10^{22}$ and come out with a small finite number, 9. The chances are you are pulling in 9 nitrogen atoms Mr. Caesar exhaled in his last breath! This scares you a little bit because a lot of people have used this air many, many times over, and what's more, we are putting things into it all the time. Of course, the air is being refreshed all the time; we are putting in pollutants all the time and removing them by the natural chemical processes that are going on.

Let us ask the same question for the oceans. We could estimate easily the volume of the ocean and we could estimate the probability of finding the same water molecules in dipping out a glassful of water, then putting it back and mixing it all up, and dipping another glassful. But we would be misled by one very important thing, namely, that the big bulk of the ocean does not in fact mix like the atmosphere in a reasonable time. By far the greatest amount of man's activity and even biological activity in the oceans is taking part in a very small fraction of it near the surface and near the coastal waters. If you were to make such an estimate for the ocean it would be necessary to consider a very much smaller volume of water than the total volume of the ocean. If we go on to the third environmental element, namely the land, we have a very, very slow process indeed of turnover and mixing. We do have, of course, a natural extraction process going on all the time in which water is being evaporated from the oceans and extracting materials from the earth. In any event, all of these environmental components are finite, and so is the total number of atoms of any chemical element essentially a constant except for a few trivial things like the radioactive elements.

Man's activities have to do essentially with two things: (1) transformation of one chemical form to another, and (2) changing the distribution of these elements, usually from rich sources such as ore deposits, into much more dilute configurations. When we start looking at the importance of the various trace metals we should consider first the abundance of these elements. In Figure 1 is the kind of listing of relative abundances that you see in many elementary chemistry textbooks. This shows the elements only in the earth's crust, and you will notice a few things--for example, that nitrogen is missing, because there is so precious little. Also, you will find that some of the metals which we regard as very common are indeed quite scarce. For example, mercury, cadmium, or lead, are relatively scarce. It is just that man has found so many uses for these metals that they have been concentrated in civilization. Conversely we find some elements, for example, titanium, that we would not regard as an important element in everyday life (except for a few things like paint pigments); it is one of the very abundant elements indeed.

Now as a generalization we can say that mainly the toxic elements tend to be the less abundant elements. That is no accident, of course, because life evolved around the abundant elements and to a large extent this table is rrelevant in that respect because life did not evolve on the average on the earth's crust. It evolved in the ocean, and there has been for a billion years or more an extraction process going on in which the elements have been extracted into the seas. Figure 2 tells us something of the distribution, in the second column, in the ocean. Unfortunately, it tells us nothing about the rare elements, but in fact practically, if not entirely, the entire list in the periodic table is present at a finite concentration in the ocean. So by and large then, we will find that the elements which are either essential to biological life or which are required in trace concentrations at least, although they might be harmful at higher concentration, are the ones that are relatively abundant. This is really outside my sphere of discussion, in the sense that this is a biological problem, but I do want to remind you that there are many, many elements then that are essential to human life and to plant life, and to animal life in general, in small concentrations that are toxic at higher ones and that we are not therefore to consider every heavy element as a pollutant and something to get rid of.

There are a good many elements for which we do not know whether they are really required at ultra-trace levels. Take for example mercury which is receiving so much attention these days as a toxic material. It has been stated recently that there may be a small residual amount which is necessary, although this has not been established to my knowledge. For our present purpose, though, mercury is essentially a foreign element and a harmful one. Likewise, I know of no physiological need for the element lead, or for cadmium, and therefore these constitute pollution problems, and as chemists we should look at the origin and distribution and so on, of these elements.

Fig. 1 - Average Composition of the Earth's Crust

Estimate of Dr. H. S. Washington

Oxygen = 46.43
Silicon = 27.77
Aluminum = 8.14
Iron = 5.12
Calcium = 3.62
Sodium = 2.85
Potassium = 2.60
Magnesium = 2.09
Titanium = 0.629
Phosphorus = 0.130
Hydrogen = 0.127
Manganese = 0.096
Fluorine = 0.077
Chlorine = 0.055
Sulfur = 0.052
Barium = 0.048
Chromium = 0.037
Zirconium = 0.028
Carbon = 0.027
Vanadium = 0.021
Nickel = 0.019
Strontium = 0.018

Lithium = 0.003
Copper = 0.002
Rare Earths = 0.001
Beryllium = 0.00XX
Cobalt = 0.00XX
Boron = 0.000X
Zinc = 0.000X
Lead = 0.000XX
Arsenic = 0.000XX
Cadmium = 0.0000XX
Tin = 0.0000XX
Mercury = 0.0000XX
Antimony = 0.0000XX
Molybdenum = 0.0000XX
Silver = 0.00000XX
Tungsten = 0.00000XX
Bismuth = 0.00000XX
Selenium = 0.000,000XX
Gold = 0.000,000XX
Bromine = 0.000,000XX
Tellurium = 0.000,000,0XX
Platinum = 0.000,000,0XX

Fig. 2 - Average Composition of Known Terrestrial Matter, Per Cent

Element	Lithosphere (93%)	Hydrosphere (7%)	Average (Including Atmosphere)
Oxygen	46.46	85.79	49.20
Silicon	27.61	.....	25.67
Aluminum	8.07	.....	7.50
Iron	5.06	.....	4.71
Magnesium	2.07	0.14	1.93
Calcium	3.64	0.05	3.39
Sodium	2.75	1.14	2.63
Potassium	2.58	0.04	2.40
Hydrogen	0.14	10.67	0.87
Titanium	0.62	.....	0.58
Carbon	0.09	0.002	0.08
Chlorine	0.05	2.07	0.19
Bromine	.....	0.008	.....
Fluorine	0.03	.....	0.03
Phosphorus	0.12	.....	0.11
Sulfur	0.06	0.09	0.06
Manganese	0.09	.....	0.09
Barium	0.04	.....	0.04
Strontium	0.02	.....	0.02
Nitrogen	.....	.....	0.03
All others	0.50	.....	0.47
	100.00	100.00	100.00

Let us turn to the next concept, which is the idea that in inanimate nature--that is, outside of life systems--a good deal of chemistry is going on, and we should bear this in mind because this is something that has nothing to do with civilization, or even life. What are these chemistries that are going on?

First is the process of distillation that I mentioned, the evaporation of sea water into the atmosphere, precipitation of rain and snow, a process of extraction from the soil and motion into the waterways and into the ocean. Action such as volcanic action, which will spew large quantities of certain chemicals into the environment--for example, gaseous pollutants like hydrogen sulfide and sulfur dioxide are emitted in huge volumes--and I will show you in a little while that we are getting definite finite amounts of metals also this way. A fourth chemical process that we can identify is the process of weathering of minerals. We have, for instance, oxidation processes going on; metals that frequently occur as insoluble sulfides are being gradually converted into sulfates and thereby become water soluble. Likewise, elemental metals are being transformed into oxides, the oxides can be converted into other salts such as carbonates which then form mineral deposits. Of course, many of our minerals are secondary minerals; they have previously been in solution, and due to changes of geological type, areas that once were under the ocean are now in land and we can find soluble as well as insoluble species existing as minerals.

There is a great deal of chemistry, then, going on all the time. I would like to illustrate this by the next family of slides. What I have chosen to do is to use mercury as sort of a pilot element, partly because of its tremendous importance these days in pollution problems and partly because so much attention has been paid that we do have data on this element where we may be lacking in similar data for other elements. This material comes from a Geological Survey publication which has recently been put out by the U. S. Geological Survey, entitled "Mercury in the Environment."

This figure (Figure 3) illustrates percentile ranges of mercury distribution. The units on the left are parts per billion and the scale is a logarithmic scale, so that we are dealing with concentrations ranging from 10 parts per billion, to over 1000 parts per billion (1 part per million) in the top range. The left-hand portion gives rock compositions on a percentile scale, 25%, 50%, 75% and 90%, which represent the percentage of the material which has less than the stated amount of mercury. These being various and sundry samples that were taken around the world for analysis, one can conclude from this that 50% of all the rock samples contain mercury in amounts greater than, say, 20 or so up to greater than several hundred parts per billion. Now the samples marked "Ivanhoe" are from a particular region of Nevada which is a mercury-rich region and represents an abnormal concentration, and actually some samples reach proportions of being commercially useful sources of mercury. The point I want to make is that there is virtually no rock

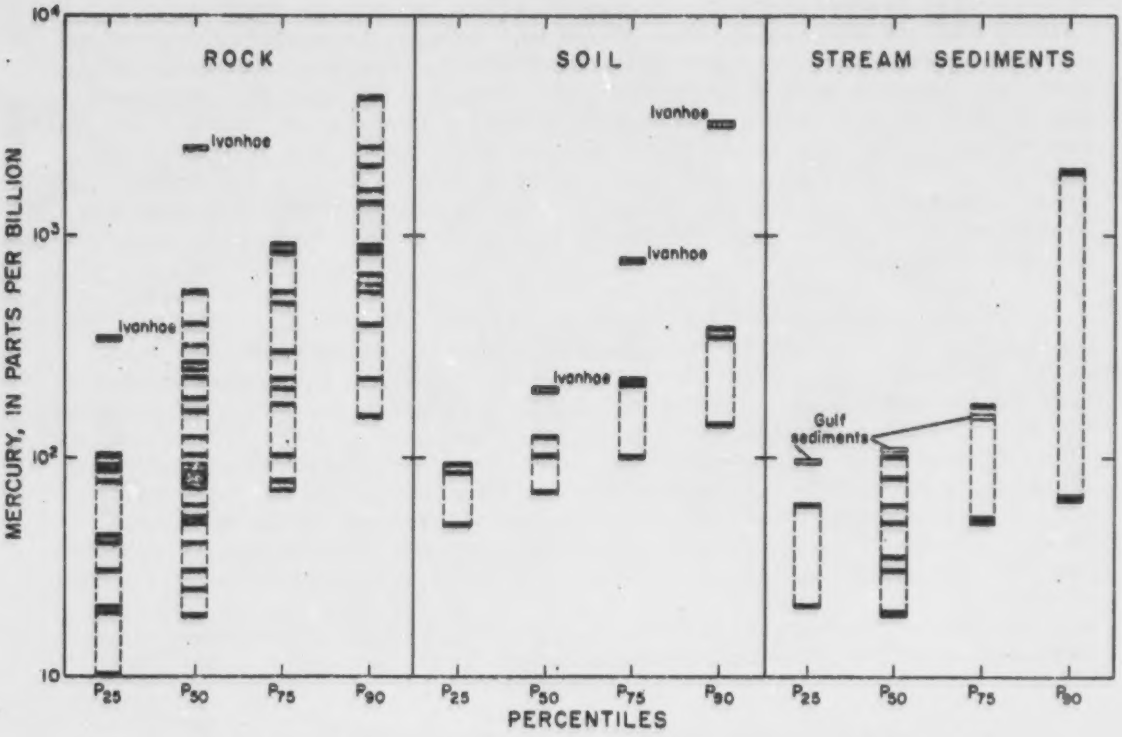

Fig. 3 - Percentile ranges of mercury distribution in rock, soil, and sediments.

whatever that has no mercury at all detectable by a modern analytical method. The middle portion of Figure 2 pertains to soil, and in much the same way as rock, soils do contain mercury in measurable and definite quantities. Mercury is not something that is constrained in nature to a few ore deposits. On the right are stream sediments with similar indications.

Figure 4 shows some data, again from Geological Survey Professional Paper 713, simply to illustrate certain data. (There are huge tables of data in this report in case you wish to study it in more depth.) The point I want to mention is that in natural waters, in units of micrograms per liter, which is parts per billion, there is absolutely no water whatever that doesn't have a detectable concentration of mercury. For example, the Pacific Ocean, even its depths, contains a certain amount, 0.2 parts per billion. Rainwater (this study was made in 1934) has 0.2 parts per billion and is typical of rainfall. Salton Sea brine is a California salt brine containing 6 parts per billion. That would be abnormally high for natural water, but amounts of the order of 0.1 to 0.2 parts per billion are not at all unusual.

Figure 5 shows something about mercury in gaseous samples. The first one is labeled "unpolluted air" and the number is 8 nanograms per cubic meter. I might say that a nanogram is 10^{-9} grams and the corresponding lead levels that we speak about are in the microgram per cubic meter range, so that if we speak about so-called unpolluted air it would have about 1000 times less mercury than lead typically. Over the Pacific Ocean, offshore 20 miles, 0.6 or 0.7 of a nanogram per cubic meter is shown. In California, a seasonal variation shows a wide variation from sample to sample. In the Chicago area, an average of 9 nanograms per cubic meter is reported. But the real punch in this particular figure is at the bottom. If we look at the air over the mercury deposit then it is certainly to be expected, because of the volatility of mercury, that there would be enhanced concentrations, and indeed on the average, 31 nanograms per cubic meter were found.

Where did all of this mercury come from then that gets spewed around so generally in nature that it is found in all the rocks and water systems? The last two entries here are very suggestive. Gases of mud volcanoes contain amounts tremendously greater than ordinary air. Volcanic gases contain relatively large amounts of mercury, but we are not about to stop a volcano! Moreover, this process has been going on for billions of years. Therefore, since mercury has been so generally distributed through nature it is not just a recent phenomenon; it is simply that in the recent past we have accentuated this process so much through our activities. I am not trying to minimize the importance of it all, but what I am trying to do is get a perspective on this subject.

This really brings me to my next theme, which is: The meaning of "zero". The reason I put it that way is, that there have been serious suggestions that *no* amount of pollution by a metal like mercury is acceptable and therefore that we should, as a legal standard, have an amount of "zero" mercury for a plant effluent or for a stack gas. The Illinois Pollution Control Board has recently considered one-half part per billion as the limit of mercury in drinking water, whereas the national standard of the U.S. Public Health Service is one order of magnitude higher, or 5 ppb. Let's do a little molecular calculation and see what we come up with. Let's take a glass of water. For purposes of convenience I am going to say a glass of water is 180 cubic cm, which is 10 moles of water. We are allowed a half a part per billion--that is, one part mercury by weight per $2x10^9$ or 2 billions parts of water. But the mercury atom weighs about ten times as much as the water molecule, so we will have to adjust this by a factor of 10 to get it on a molecular basis. We multiply this by the number of molecules of water and we get a number which is $3x10^{14}$. That is how many mercury atoms we are allowing our glass of drinking water to have. If we divide this by the population of the country, which is around 200 million, or $2x10^8$, we come out with 1-1/2 million mercury atoms per capita. Now that is a horrifying thought, isn't it? That is ten times the stringency of the national standard. Are we to then conclude from this that the Illinois State Board is being lax and therefore should tighten its standards enough so that we don't have any of these?--maybe one per capita?

Now we are getting into the realm of the meaning of "zero". If we are to put a standard of zero effluent mercury content in an effluent, what we really are saying is an *undetectable* amount in the effluent, and when we say that, we must specify the method that we use in order to try to detect it and fail. Not only must we define the method in general terms, such as neutron activation analysis, or something of the sort, but we have to specify precisely the way that this is done, the equipment that is to be used, etc.; or you can do it in a sloppy way and fail to find it. A chemist that is pretty clever can manage to make a test fail, so you must be very careful to specify exactly how that test should be done. Why is this done? It really is an effort to make it quantitative. They don't want to say that there is a finite limit; they want to make such limits zero, but they don't want to specify what that limit would be and therefore they will specify the method. So it is totally futile in the first place then to have a "zero" limit; it will not be zero, it will be the detection limit. The most sensitive analytical method I am aware of is one that will detect about 1,000 atoms on a microscopic speck of sample, not in a gallon of water.

Now I would like to take the liberty of reading a paragraph in an editorial I wrote. Each month I wrote an editorial for the journal, "Analytical Chemistry", and this will appear in April, "The Meaning of Zero." In the final paragraph I said as follows:

> "Most important of all, the sensitivity of an analytical method is not a rational basis for a pollution standard. Even if zero pollution were achievable and testable, the cost of reaching such a goal could be largely wasted once the levels of purity existing in nature undisturbed by civilization have

Fig. 4 - Average Mercury Content of Natural Waters *

Micrograms per liter

Rhine River, 1934	0.1
Elbe River, 1957	0.09
Armenian SSR, 1963	4.2
Atlantic Ocean, 1963	1.2
Pacific Ocean, Ramapo deep, 1961	0.2
Minimata Bay, Japan, 1961	1.6 - 3.6
Rainwater, 1934	0.2
Salton Sea brine, 1967	6

Fig. 5 - Mercury in Air and Volcanic Emanations *

Nanograms per cubic meter

	Min.	Max.	Average
"Unpolluted air," 1934	.....	.....	8
Over Pacific Ocean, 20 miles offshore, 1968	0.6	0.7	
California, winter, 1968	1	25	
California, summer, 1968	1.5	50	
Chicago area, 1969	3	39	9.7
Over mercury deposit, 1969	12	57.5	31.4
Gases of mud volcanoes, 1966	700	2000	
Gases, Mendeleev and Sheveluch volcanoes, 1966			

* Source: Geological Survey Professional Paper 713, "Mercury in the Environment," 1970.

> been passed. For life evolved and developed in a real world, but natural processes of extraction, distillation, etc., have introduced finite amounts of all elements into the ocean. For man-made chemicals the problem is different. Even here the rational basis should be detectable damage, not an indefinable and unreachable zero."

In other words, to a chemist "zero" means no molecules at all. But a chemist is unable to detect a single molecule, and therefore this is unreachable and undefinable. That is the point I wish to make.

The next point I would like to stress is: The importance of the chemical form of the element, not just the element. Now we are going to take three examples. The first of these is mercury, again, and this will be stressed a great deal more by John Wood next week, so I will not presume to take his topic away from him. I want merely to use this as an example of the importance of chemical form, because when we make a pollution standard such as a "half-part per billion of mercury" we specify the total amount of this element. And yet we should distinguish chemically between mercury itself, the element, mercurous ion or Mercury(I), Mercury (II) or mercuric ion, methyl mercury, dimethyl mercury, and of course there could be many, many other forms of organic mercury such as phenyl mercury, but these are the important ones in environmental terms. Now the message, of course, is that some of these are more harmful physiologically than others. Therefore, we really should be putting our attention on limits for things, like the organic form rather than the total mercury.

Of course, you can argue that out in nature we have processes that will convert inorganic to organic mercury, so we are on the safe side if we specify the total. It is just that there is going to be already a certain amount of mercury in the environment that we cannot escape and that man has lived with long before civilization crept in; and really, it is important to tell something about the form in order to describe the gravity of the hazard. People often do not realize that metallic mercury itself without being oxidized is soluble to a finite extent in water. At room temperature that solubility corresponds to 25 ppb, which is 50 times the proposed drinking water standard here. I am going to let the chemists here ponder how you would remove mercuric ion to levels below that, (and there are ways, notably adsorption on activated charcoal or even on naturally occurring sediments in water). But clearly we cannot even allow a saturated solution of metallic mercury then to be around if we are to meet such standards. Of course, beyond that there is a great deal higher solubility when oxygen enters the picture and we can oxidize metallic mercury to mercurous or mercuric forms.

Figure 6 tells us something about the inventory of mercury. This is a useful starting point, for the reason that it gives us some measure of the size of the problem in terms of industry. For many metals we have such sources, and I won't presume to put them all forth, but this was taken from Chemical and Engineering News of last year.* These are in thousands of pounds of mercury. The total consumption was 6 million pounds in this country--a rather horrifying thought when you think of it in terms of what that could do to the environment if it were all distributed, say, as methyl mercury. Electrolytic chlorine is at the top; this is, of course, the source from which much of the contamination in the Great Lakes has come (and not because it was necessary, but because people were ignorant of how important it was). There have been cleanup procedures, at least as far as the plant effluents are concerned, instituted in recent times, so the problem is not really growing; but it is still there in large quantities, as professor Wood will tell us.

I would call your attention to dental preparations--209,000 pounds of mercury were going into that and that is going into your mouth. As long ago as 1930 there was some serious question about the physiological importance of this mercury. There were several important studies** made in Germany in the period of the 1930's. Mercury analyses were taken on people that had no mercury fillings as well as those who did. It was con cluded then that the total ingestion rate of mercury in all of your food was in the order of 5 micrograms per day, and that this was also the rate at which you were emitting mercury mainly in the urine. If you had a dental filling made you could see an upsurge in the mercury excretion from your body; this could be traced for several months. Even 18 months later you could get a noticeable increase over the background of mercury emissions from your body. If we are to become purists about this, the first thing we should do is get our amalgam fillings yanked out. But I don't say seriously that this is what you need to do. My mouth is full of them and I am not terribly concerned about it because I feel that in terms of the amount I am taking unavoidably in all of the foods that I eat that will not be a large increment from that; and therefore I am not worried, particularly because this is inorganic mercury. Furthermore, I will eat some tunafish now and then, although I would not eat it every day for every meal because this mercury is in the more toxic organic form. What about eggs? (from audience) That all depends. There is a history of really serious contamination through poultry eating seed grain that had been treated with methyl mercury and then eggs could become contaminated. If they get such grain, yes; but if not, there is no such danger.

Figure 7 is on mercury also. This is from Environmental Science and Technology--and I refer you to this journal as an important literature source for technical information. Now the only point I want to make in that is, that if you were to carry out an inventory for a period of time like 1945-1958, 678,000 mercury flasks were consumed in this country over that period. If you run a material balance there is a discrepancy

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* C.&E.N., June 22, 1970.

** P. Borinski, Klin. Wochschrifte, 10, 149 (1931); Cf. Chem. Abstr. 26, 2504 (1932); A. Stock et. al., Z. anorg. Allg. Chem. 217, 241 (1934); Naturwissenschaften, 22, 390 (1934).

Fig. 6 - Mercury Consumption in U.S. tops 6 million pounds

1969 Consumption
(Thousands of pounds)

Electrolytic chlorine	1572
Electrical apparatus	1382
Paint	739
Instruments	391
Catalysts	221
Dental preparations	209
Agriculture	204
General laboratory use	126
Pharmaceuticals	52
Pulp and paper making	42
Amalgamation	15
Other	1082
Total	6035

Note: Consumption based on 76-pound flasks.

Source: U.S. Department of Interior, Bureau of Mines.

Fig. 7 - U.S. Mercury Inventory *
(in 76-lb. flasks)

Year	Production +	Import -	Export -	Consump. -	Change in Inventory =	Discrepancy
1945	30,800	68,600	1,000	62,400	3,000	-33,000
1950	4,500	56,000	400	49,200	14,600	3,700
1955	19,000	20,400	500	57,200	-12,500	5,800
1945-58	274,200	683,400	10,500	678,200	-45,800	-314,700

* From E.S.T. 4, 890 (1970)

of 314,000 flasks that is unaccounted for. Nobody knows whatever happened to that. It is scattered around someplace, and it is going to be a wicked, really a vicious problem, to get it back out.... But let us keep the problem in perspective.

Figure 8 deals with lead. In the same way as in the other this shows the lead consumption in tons. To give you an order of magnitude for the problem in 1969 it is divided into metal products, pigments, gasoline additives and miscellaneous. Now to a large extent this represents a recycling of lead; that is, the storage batteries are not consumed, they are reused. This is a misleading balance of consumption in that respect. What I want to refer you to specifically is gasoline additives, which means essentially tetraethyl lead. A huge amount, 271,000 tons, goes into the atmosphere and every bit of that does wind up in the environment. We must be concerned from the sheer magnitude of the problem. Again, we should do this in the perspective of how harmful it is, not just how much is there?

This, then, encourages me to tell about the importance of chemical form once again. We start out in the gasolines with tetraethyl lead. This is added with organic bromine and chlorine compounds to the gasoline as tetraethyl fluid. This is combusted and emitted into the atomosphere as microcrystals of lead chlorobromide, with minor amounts of other lead compounds. For example, a phosphate additive in gasoline comes out as lead phosphate, which is a very insoluble compound. This is the principal form. Now, what do the lead halides do? They enter the water system where they are soluble to the tune of almost 9 grams per liter. They will readily dissolve and give you lead ions in the water. The mysterious thing is that if you look into most natural waters and look for the lead (and we'll have some speakers on this subject later in the series) you'll find that to a large extent the lead has disappeared.

It seems likely that the way the lead disappeared was in fact upon clay. Clay is a natural ion-exchanging material which is present not only in soil but also in natural waters as sediment. In fact, it is pretty hard to find natural water that does not have some clay with ion exchange capacity sufficient to tie up lead and other heavy metals. So we have then a lead-clay complex. There are other kinds of natural complexing agents. (Professor Bailar later in the semester will tell us something about the importance of complexing agents with respect to metals in the environment.) So nature does have a way of protecting us, in a way, from our own folly as it were. The question, though, that is unanswered as far as I am concerned is: really how effective is this protection mechanism? There needs to be a great deal more research into finding out, for example, whether the plant really will be protected. And the indications are that we are lucky; that indeed the plants do not take up much lead from the soil just so long as there is clay in the soil to tie up the lead.

Similarly, there is an inverse association between lead uptake and phosphate content, both in water and soil. High phosphate water then, which, mind you, is considered a form of pollution these days, could actually help in suppressing the lead level. The mechanism of that is, as far as I am aware, unknown. It is often described as a precipitation. This is unlikely to be so at the levels of concentration we're dealing with; it is perhaps a complexation.

Another example of the importance of chemical form I'd like just to mention very briefly is in the case of chromium. Chromate ion is used in large quantities as a corrosion inhibitor for iron. It is one of the best. It is used in practically every system in which cooling water is used in metal types of condensers. Now some of that inevitably gets into the environment, either through leaks or through other mechanisms. Chromate (or chromium VI, or hexavalent chromium) is very, very toxic, at least a hundred times more toxic than trivalent chromium. And therefore the chemist, if he can devise a scheme in which this hexavalent chromium is reduced to the trivalent form, will be doing a good job. He will improve the water considerably, without ever removing the chromium physically. And there are many, many other examples I won't presume to try to cover today, but I want you to keep in mind that principle of the importance of the chemical form. Don't think just in terms of elements; think in terms of chemical species.

Now the next principle I would like to mention is the problem of chemical reactions at high dilution. There are two general chemical principles that come to bear here. If we are trying to do chemistry under a very low concentration, whether in the atmosphere or in the water for example, there are two general things that happen. First, reaction rates are generally proportional to the concentration and therefore at very high dilution ordinary chemical reactions slow down. The second point is that the completeness of the reaction (the thermodynamics of the reaction) generally also becomes unfavorable at high dilution. And what this leads to in terms of pollution control is, that you should do your chemistry nearest the source wherever the pollution concentration is the highest, there is where you should do your abatement procedure. Don't wait until it's mixed up in the lake or in the ocean and then try to do something about it. Try to hit it before that time.

The next chemical principle I'd like to mention is the usefulness of the periodic table. The chemist commonly uses the periodic table as a method of guessing the chemistry of a similar element from the known chemistry of another element. For this I would like to use the example of cadmium and zinc. Figure 9 shows a table taken from a recent article in Environmental Science and Technology which spoke of roadside contamination with trace metals. Now I should tell you that the farther you get away from the road in this case the less contamination from any of these metals. The inescapable conclusion is that somehow these metals derive from the automobile which was using the road. In the case of lead it is directly traceable to the lead in the gasoline. In the case of nickel it is traceable to the nickel alloys which are used in various parts of the automobile --for example, the exhaust system which is corroding. The zinc and the cadmium, though, cannot be traced to the metallic parts of the automobile

Fig. 8 - Lead Consumption in the United States (1969)
(in short tons)

Metal Products:	
Storage battery oxides	295,337
Storage battery grids, posts, etc.	262,784
Ammunition	77,805
Solder	65,126
Cable covering	54,078
Other	172,754
Total	927,884
Pigments:	
Red lead and litharge	79,934
Other	21,952
Total	101,886
Gasoline Additives	271,128
Miscellaneous Uses	32,305
Grand Total (a)	1,333,203

(a) Includes lead content of scrap used directly in fabricated products.

Fig. 9 - Roadside Contamination with Trace Metals

16 meters from road, mg/kg dry weight

Element	Grass	Soil Profile Layer 0-5 cm	5-10 cm
Cd	0.73	0.40	0.38
Ni	3.8	2.4	0.9
Pb	47.5	378	260
Zn	28.5	66	48

From: J. V. Lagerwerff and A. W. Specht, E.S.T. 4, 583 (1970).

despite the fact that there are definite amounts of zinc and cadmium used as metal; it is traced to the rubber tires of the automobile. Zinc oxide is used as a compounding agent in the vulcanization of rubber. The cadmium is an impurity in the zinc and comes along with it. If, therefore, we were to attack this problem the proper way would be to attack it thru using a higher grade of zinc oxide in the rubber vulcanization process. Cadmium is a very poisonous element, but there has been very little done yet on this element and it is our plan here at Illinois in our interdisciplinary project to focus on cadmium as one of the next targets after we learn how to operate on some of these environmental samples of lead. And another little statistic on cadmium and zinc you might be interested in is this: whole wheat flour has a ratio of cadmium: zinc of 1 to 120--about the natural ratio that you find in most ore. When whole wheat flour is refined and we have white flour, it turns out that you are enriching the cadmium relatively to zinc and now the ratio is one part of cadmium to 20 parts of zinc. You have lost by a factor of 6 with respect to this cadmium: zinc ratio. Zinc, you see, is an essential element although it is toxic at very high concentrations, and when present in adequate amounts it protects to some extent against the toxicity of cadmium. On the other hand, cadmium, as far as I know, is not essential at all. Maybe the biologists can tell us differently.

Another periodic relationship is arsenic-phosphorus. These are in the same group of the periodic table. Phosphorus, as you well know, is used in detergents as a builder and there is quite a bit of discussion on this subject at the moment. However, this is not one of our principal subjects of this seminar, because phosphorus happens to be a non-metal, and besides, phosphate is not a pollutant in the sense of being a poison. It is a pollutant in the sense of being a plant nutrient. However, arsenic does occur in nature with phosphorus in phosphate deposits, but not uniformly in all phosphate deposits. Merely by collecting phosphate on the basis of arsenic content, we can avoid this contaminant very largely without using any chemistry to separate it.

Another example of periodic relationships that are useful is in the second group of the periodic table where we find the elements magnesium, calcium, barium, and radium. These are similar chemically. Calcium, of course, is an important component of our bodies, of our teeth, and our bones particularly. So radium, if it is ingested, happens to be toxic primarily because it is radioactive, not because of its chemical toxicity; but nonetheless it finds its way into the bones and it becomes particularly noxious because of its tendency to do that, because it is chemically similar to calcium. Strontium 90 has likewise received a lot of attention in the fall-out days of nuclear weapons testing, because of its chemical similarity to calcium and, again, its retention in the bones.

I want to close with one final note. That note is the question: Is there technology already in existence to take care of our problems or not? I would answer it in the following way. We have a great deal of technology that has not yet been put to use in pollution abatement. However, to a large extent this is uneconomical technology. We need a great deal more in the way of research to decide what abatement measures are necessary and to make these measures more economical so we can afford it. We haven't yet faced the cost of these abatement measures. There is need for more work in understanding the chemistry of these materials, the biology of these materials, and especially the interactions between several types of pollutants present in marginal amounts. More work is needed in identification of the species, in handling the data that we get from modern analytical methods. The automated methods that we are developing will spew out such large numbers of data that we need computer facilities simply to store and make that data available to other people.

And so I must then conclude by saying that, while we do have a great deal of technology available, there is still a vital need for both research and development in the area of environmental pollution.

HEAVY METALS AS ENVIRONMENTAL POLLUTANTS

R. L. Metcalf

Introduction

The technology of heavy metals is the backbone of our civilization which has been based successively on lead, copper, iron, aluminum, magnesium, and titanium as marking the progress of man from anthropoid to astronaut. Today our industrial effort is centered around not only these key elements, but also a number of subsidiary but virtually indispensable metals, including antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, manganese, mercury, molybdenum, nickel, platinum, selenium, silver, strontium, tin, uranium and vanadium. As shown in Table 1, the United States is the world's major consumer of heavy metals.

During the past 100 years of the industrial revolution, man's insatiable need for raw materials has removed a very substantial proportion of the metallic ores from their sequestered and generally chemically combined forms as oxides or sulfides and has mobilized them through metalurgical processes or inadvertently through smelting and the combustion of fossil fuels so that they have become global pollutants. As an example of the exponential growth of contamination, the rates of mobilization of lead as shown in Table 2 are highly informative.

Within the past 40 years the increasing production and use of metalo organic compounds such as the lead alkyl gasoline additives, methyl and mercurial fungicides, slimicides, antifouling paints, and organoarsenic and organotin pesticides have provided an additional avenue for environmental pollution.

The accumulating impact of these industrial activities on the environment has not been well recorded. Here and there small bits of evidence afford us exploratory glimpses of pollution problems of great magnitude for which urgent solutions are needed.

Water pollution by trace metals is clearly extensive. Recent surveys in rivers and lakes of the United States (Kopp and Kroner, 1967, and Durum *et al*., 1970) produced the results shown in Table 3. The rates of accumulation of heavy metals in Lake Michigan are even more informative (Table 4). The increasing concentrations in top levels of sediments reflect industrial mobilization of the heavy metals.

Perhaps the most dramatic illustration of the mobility of heavy metal contamination is the amounts found in sewage sludge (Table 5).

It is evident from the foregoing brief summary that through the impact of the "Industrial Revolution" man has succeeded in contaminating the biosphere with a large variety of metals and their cations which are present in the water we drink, the food we eat, and even in the air that

Table 1

U.S. Consumption of Heavy Metals - 1968

(Minerals Yearbook 1968)

Metal	U.S. Consumption (lbs)	Percent of World Production
Arsenic	50,390,000	39
Antimony	37,040,000	27
Beryllium (as beryl)	17,438,000	99
Bismuth	2,347,768	31
Cadmium	13,328,000	43
Chromium	2,632,000,000	25
Cobalt	13,000,000	30
Copper	2,469,448,000	19
Columbium and Tantalum	4,828,000	24
Lead	2,657,580,000	40
Manganese (35%)	4,445,824,000	12
Mercury	5,732,072	30
Molybdenum	75,647,000	60
Nickel	318,612,000	30
Platinum Group	113,992	40
Selenium	941,000	46
Silver	15,177,100	67
Tin	185,592,640	36
Titanium (conc.)	2,552,472,000	36
Tungsten	11,038,000	16
Uranium	24,676,000	55
Vanadium	10,990,000	44
Zinc	3,456,800,000	34

Table 2

10^3 Metric Tons Lead Smelted or Burned per year

Murozumi et al., (1969)

Date	Northern Hemisphere Smelted	Northern Hemisphere Burned as alkyl-leads	Southern Hemisphere Smelted
1750	60		40
1800	90		50
1860	220		
1900	750		80
1910	1000		100
1920	1080	0	110
1930	1600	4	170
1940	1700	36	230
1950	1850	110	240
1960	2500	180 (1958)	360
1966	3100	310	350

Table 3

Trace Element Concentrations in Surface Water of United States

Koop & Kromer, (1967)

Element	No. Positives	Frequency %	Range ppb	Violations[1]
Aluminium	456	31.2	102760 (74 mean)	
Arsenic	87	5.5	5-336 (64)	41
Arsenic[2]	153	21.0	10-1.100	14
Barium	1568	99.4	2-340 (43)	
Beryllium	85	5.4	0.01-1.22 (0.19)	
Cadmium	40	2.5	1-120 (9.5)	6
Cadmium[2]	305	42.0	1-130	29
Chromium^{+6}	386	24.5	1-112 (9.7)	4
Chromium^{+6} [2]	80	11.0	6-50	
Cobalt	44	2.8	1-48 (17)	
Cobalt[2]	269	37.0	1-4.500	
Copper	1173	74.4	1-280 (15)	
Iron	1192	75.6	1-4600 (52)	25
Lead	305	19.3	2-140 (23)	27
Lead[2]	458	63.0	1-890	3
Manganese	810	51.4	0.3-3230 (58)	74
Mercury[3]	39	49.3	0.1-17 (1.04)	
Dissolved[2]	51		0.1-4.3	
Total	51	71.0	0.1-6.8	
Molybdenum	516	32.7	2-1500 (68)	
Nickel	256	16.2	10130 (19)	
Silver	104	6.6	0.1-38 (2.6)	
Strontium	1571	99.6	3-5000 (217)	
Vanadium	54	3.4	2-300 (40)	
Zinc	581	80.0	5-42,000	2

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[1] Values in excess of recommended Federal Water Quality Standards: arsenic 50, cadmium 10, chromium 50, iron 300, lead 50, manganese 50, mercury 5, and zinc 5000 ppb.

[2] Durum et al., (1970).

[3] U.S. Geol. Surv. Prof. Paper 713 (1970).

Table 4

Accumulation of Heavy Metals in Bottom Sediments of Lake Michigan

Shimp et al., (1970), Ruch et al., (1970)

Element	Concentration in ppm at indicated Depth in cm[1] 0-3	3-6	6-8	8-10.5	10.5-13.5
arsenic	13	5.1	7.5	9.4	4.5
cadmium	17	7	5	5	
chromium	64	37	30	40	
cobalt	10	8	9	11	
copper	109	26	23	21	
lead	90	19	18	18	
nickel	35	26	27	26	
vanadium	54	34	32	36	
zinc	179	42	46	50	

[1] Station 44 - 12 miles east of Waukegan, Ill.

Table 5

Trace Metals in Sewage Sludge, Chicago

Horn, (1970)

Element	range	average
cadmium	1-110	22
chromium	25-580	181
cobalt	non-detected	
copper	24-690	143
iron	661-9740	2297
lead	6-510	98
manganese	5-143	48
molybdenum	0-0.06	
nickel	trace-150	30
zinc	90-2280	

we breathe. Apart from any considerations of public health, the magnitude and nature of trace metal contamination in various segments of the ecosystem are important facets of ecological biochemistry. However, it has been known since antiquity that certain of the trace metals are highly toxic to many forms of plant and animal life and, indeed, the Borgias of the Middle Ages with their poisonous elixirs of mercury, lead, and arsenic salts were but the predecessors of the enzyme chemist of today who uses mercury salts to inhibit sulfhydryl enzymes, arsenite to block triose phosphate dehydrogenase, and lead salts to block porphyrin synthesis.

Although there are a number of trace metals which are essential to life as prosthetic groups for enzymes and as oxygen carriers in respiratory pigments, including Fe, Mg, Co, Mo, Mn, V, Zn, and Se, there is a smaller group including Hg, Pb, As, Cd and Sb which seems to have no essential interactions with living systems and whose presence and accumulation in living organisms and their substrates is wholly deleterious. There are grave deficiencies in our knowledge of the environmental distribution, ecological interactions and public health consequences of our widespread industrial usage of these metals. This is emphasized in the following discussion.

Lead as an Environmental Pollutant

Lead is one of the important industrial metals and the world production in 1966 was 5.99 billion pounds, of which 2.66 billion pounds, or about 44%, was consumed in the United States. Data from the Bureau of Mines Yearbooks, summarized in Table 6, show the various industrial uses and the rates of increased utilization over the past 30 years. Almost 63% of the total lead is consumed by the automobile industry, with 18.2% going into gasoline additives and 37.3% into storage batteries. The U.S. consumption is approximately 15 pounds per capita, and because of the durability of lead it is suggested that perhaps 25 times the annual consumption is in usage. Some of the lead is released into the environment from all forms of industrial activity and this loss is estimated to be 0.01-0.1% of the total production, or 250,000 to 2,500,000 pounds annually in the U.S. (First, 1966). Such release is generally localized in the vicinity of smelters and reclamation plants.

Another important source of environmental contamination is lead ammunition--especially bird shot, which is an important source of lead poisoning in migratory waterfowl. Bellrose (1959) has suggested that 1,400 No.6 lead shot find their way into the environment for every duck killed, and well over 100,000 pellets have been found per acre of lake bottom.

Lead has long been used in paints, and Patterson (1965) estimated that 3.4 trillion g of lead--largely as white lead, $Pb_3(OH)_2(CO_3)_2$, and chrome yellow, $Pb(CrO4)_3$, have been applied in the U.S., largely as exterior paint. Although the annual rate of application of leaded paints has diminished to about 0.2% of the rate of 40 years ago, Patterson suggests that the ablation of paint residues should have elevated the concentration of lead in urban soils from 15 to 600 ppm.

Lead arsenate, $PbHAsO_4$, has been widely used as an insecticide. Some 85.5 million pounds were produced in the U.S. in 1944, but the amount has declined to the 8 million pounds produced in 1966 (USDA statistics) and this important source of environmental pollution is being drastically curtailed.

The most direct source of environmental pollution by lead is throug the combustion of lead tetraethyl gasoline additives which are directly emitted to the air over most of the U.S. in the form of water-soluble lead halides. The rapidly-increasing amount of lead used in this form presently comprises about 18% of the total U.S. lead consumption.

Table 6

Industrial Consumption of Lead in the United States

U.S. Bureau of Mines, Minerals Yearbooks

	Million Pounds						
	1934	1944	1954	1964	1965	1966	1967
lead tetraethyl (gasoline additive)	--	170	320	448	450	493	494
batteries	326	614	674	859	910	1044	933
solder	14	41	142	142	156	158	138
ammunition	70	126	80	113	115	156	157
type metal	26	46	52	51	--	--	57
brass and bronze	--	--	40	46	--	--	41
miscellaneous metal products	540	123	882	745	333	537	459
pigments	--	--	--	--	218	240	103
Total	976	1120	2190	2404	2482	2648	2521

Two modern analytical studies have shown dramatically that modern industrial activity, especially the combustion of tetra-alkyl leads, has greatly increased environmental pollution by lead. Patterson (1968) evaluated the lead concentration in the North polar snows and found that the level in ice laid down in 800 B.C. of 8 g per ton was increased to 90 g per ton in 1950, and 210 g per ton in 1965. Schroeder and Balassa (1961) measured lead deposited in the annual rings of an elm tree growing about 50 meters from a lightly-traveled suburban street. The concentrations of lead in ppm averaged: 1865-79, 0.16; 1900-12, 0.12; 1940-47, 0.33; 1956-59, 0.74; and the bark and cambium in 1960, 3.9. As a result of detailed considerations of the total environmental contamination of the United States by lead, Patterson (1965) has concluded that "the industrial use of lead today is so massive that the amount of lead mined and introduced into our relatively small urban environments is more than 100 times greater than the amount of natural lead leached from the soil by streams and added to the oceans over the entire earth....and that the atmosphere of the northern hemisphere contains about 1000 times more than natural amounts of lead."

Lead Pollution from Gasoline Additives

A major pathway for environmental pollution by lead is through the use of tetraethyl lead as an anti-knock additive in gasoline. This use is increasing at a rate of more than 5% annually. The increase in the number of automobiles, gasoline consumption, and tetraethyl lead follow the same pattern. The gasoline used in automobiles has an average tetraethyl lead content of 2.1 g per gallon, and special blends may contain as much as 3 ml of tetraethyl lead per gallon (Chow and Johnstone, 1965). Tetraethyl lead contains 1.057 g lead per ml (Hirschler *et al*., 1957). There is combusted annually in automobiles of the U.S. about 493 million pounds of lead (Bureau of Mines, Minerals Yearbook). The substantial rate of increased use is suggested by *Chemical and Engineering News* (March 3, 1970, p. 42): "Each gallon of today's gasoline has about 4 grams of lead in it, which adds up to 700 million pounds of lead consumed each year by gasoline sales."

Belated social concern about lead pollution has led to lowering of compression ratios in most 1971 automobiles, equipping them to run on lead-free gasoline. This should not only begin to decrease lead pollution but also will prevent lead poisoning of catalytic converters, and will therefore be an important step in air pollution control. However, the technological problems of gasoline conversion to non-lead fuels and the gradual replacement of the 105 million high-compression engines in today's vehicles is a stupendous undertaking which will require a "long period of time, perhaps up to 10 years" (Chemical and Engineering News, March 16, 1970, p. 38). Meanwhile, the United States will be blanketed with an estimated additional 4 billion pounds of lead which will enter into the global ecosystem. Therefore, the urgency for the study and evaluation of the consequences of lead pollution from gasoline is in no way diminished by the presently-voiced concerns about changes in the technology of motor vehicle fuels. Indeed, the contemplated drastic changes in the technology of a multi-billion-dollar industry provide an exceptional opportunity for the study of the broad social interactions involved in the economic, sociological, political, legal, and public health interrelations posed by Society's attempt to correct a classic pollution problem.

From 70 to 80 percent of the lead in gasoline is discharged in automobile exhaust gases over a 20,000 to 30,000 mile driving period and the remainder, apparently trapped in lubricating oil and oil filters or retained in the exhaust gases, is variable and greatest at high speeds and under maximum acceleration. The lead is released in aerosol form with particles ranging from 0.01 micron to several milimeters in diameter. Typically, less than 5% of the lead is in particles less than 1 micron in diameter. In city driving, 27%, and in acceleration 39% was found to be in particles greater than 5 microns in diameter (Hirschler et al., 1957). However, Goldsmith (1969) reports analyses of lead atmospheric particles showing 50 to 80% by weight in particles of $< 1\ \mu$ diameter, and Muniak (1970) states that the mass median diameter of lead aerosols in auto exhaust is about 0.2μ. The particle size characteristics of lead aerosols are important due to the retention characteristics in the human lung. This has been suggested by Goldsmith (1969) to be 25 to 50% for lead aerosols from automobile exhausts.

Gasoline contains substantial amounts of ethylene dichloride and ethylene dibromide "scavengers" to prevent the accumulation of lead oxide in the engine combustion chamber. Tri-cresyl phosphate and other phosphorus compounds may also be added to prevent deposits. These additives convert the exhausted lead to a complex mixture of compounds in which lead halides are predominant. Hirschler et al., (1957) determined the composition of exhaust aerosol particles by X-ray diffraction and found 30 to 90 percent as $PbCl\cdot Br$, and 10 to 40 percent as $\alpha\text{-}NH_4Cl\text{-}2PbCl\cdot Br$ and 5 to 35 percent $\beta\text{-}NH_4Cl\text{-}2PbCl\cdot Br$. Smaller amounts of $2NH_4Cl\text{-}PbCl\cdot Br$ were found and, when phosphate additives were present, $3Pb_3(PO_4)_2\text{-}PbCl\cdot Br$. Under conditions of maximum acceleration 85 to 90 percent of the exhausted aerosol was $PbCl\cdot Br$. The water solubility of $PbCl\cdot Br$ should be intermediate between $PbCl_2$ (0.99 g/100 ml) and $PbBr_2$ (0.844 g/100 ml). Therefore, most of the exhausted lead should dissolve in rainwater and contaminate streams, rivers and lakes.

Half of the U.S. passenger automobile miles are driven in urban areas and Patterson (1965) has calculated that the effective volume of the urban area ($6\text{x}10^{10}m^2$) is about $6\text{x}10^{13}m^3$. Based on the combustion of $4\text{x}10^{10}$ g Pb/year to form stable aerosols on a 12-hour day, the average urban atmosphere contamination by lead from tetra-alkalyl lead is about 0.6 μg Pb/m^3. This compares with the average urban values of 0.5-1.4 μg Pb/m^3 found in the National Air-Sampling Network of the U.S. Department of Health, Education and Welfare (McCaldin, 1966). The mean daily average in New York City air is 7.5 $\mu g/cm^2$ and 2-hour values as high as 34 $\mu g/m^3$ have been measured (Bove and Siebenberg, 1970). Urban air pollution with lead is directly related to traffic volume and may range up to 50 to 100 times the average rates in heavily congested areas as shown in Table 7. The maximum values found of 30-44 $\mu g/m^3$ should be compared with the occupational health standards for exposure to lead in air of 150 $\mu g/m^3$. However, the National Air Quality Limit proposed by the American Industrial Hygiene Association is 10 $\mu g/m^3$, and Montana and Pennsylvania have set a maximum tolerable level of 5 $\mu g/m^3$. European regulations are much more restrictive. The maximum permissible level for exposure of the general population is 0.7 μg/m^3 in the Soviet Union, while Germany has a tentative level of 2 μg/m^3 (Danielson, 1970).

Table 7

Summary of Lead in Atmosphere in U.S. Cities

(McCaldin, 1966)

mean Pb μg/m^3	location
0.3	suburban stations 1954-56
0.5	urban stations 1957-1960
0.8	urban stations 1959-1962
1.4	annual average 4 stations, Cincinnati
1.6	annual average 8 stations, Philadelphia
2.5	annual average 8 stations, Los Angeles
4.7	parked in residential street, Cincinnati
7.7	parked by heavy traffic, Cincinnati
11.5	driving downtown during afternoon rush, Cincinnati
15.1	driving in heavy traffic, Cincinnati
21.5	driving freeway traffic weekday, midday, Los Angeles
24.1	parked along freeway, weekday, midday, Los Angeles
29.3	driving freeway traffic, morning rush, Los Angeles
38.0	parked in major freeway, weekday, morning rush, Los Angeles
44.5	Sumner Tunnel, outlet air, Boston

The washout of lead aersols and leaching of lead-contaminated soils contributes lead to surface water supplies. Patterson (1965), from geochemical considerations, calculates the natural concentration of lead in fresh surface waters to be 0.0005 ppm. Actual measurements are available from extensive Federal Water Pollution Control Investigations. Ettinger (1968) recorded values for lead in unfiltered surface waters in the Detroit River as ranging from 0.01 to 0.1 ppm, with most values from 0.01-0.02 ppm. In the Illinois River system 30 of 80 samples showed more than 0.05 ppm, with values in industrial tributaries of up to 0.18 ppm. Dissolved lead in filtered surface waters as determined over 1962-65 was generally below the 1962 U.S.P.H.S. Drinking Water Standard of 0.05 ppm. Five samples were found in the range of 0.053-0.091 ppm and were associated with industrial operation. Additional nationwide analyses of drinking-water samples during 1963-65 showed that of 531 samples, 465 had less than 0.01 ppm Pb, 12 from 0.02-0.029 ppm, and only 4 from 0.03 to 0.039 ppm. A few analyses of rainwater showed 3 of 23 samples to contain greater than 0.05 ppm Pb, while samples collected in an urban area near a busy highway contained up to 0.21-0.49 ppm Pb (Ettinger, 1966). Some natural waters in regions containing limestone and galena contain as much as 0.4-0.8 ppm Pb in solution (McKee and Wolfe, 1963).

The solubility of lead in water is determined by factors such as comparative absence of Ca and Mg bicarbonates (i.e., hardness), low pH, high dissolved oxygen, and high nitrate content (McKee and Wolfe, 1963). It should be pointed out that most of the lead liberated through air pollution is in the form of the relatively-soluble $PbCl \cdot Br$.

Sewage in the U.S. has been estimated by Patterson (1965) to contain $8x10^9$ g Pb/year. However, secondary treatment of sewage has been inferred to remove about 50 percent and the primary treatment about 15 percent of lead. However, the sewage sludge produced may contain from 0.215 to 0.78 percent lead which can again add to soil contamination after its disposal (Ettinger, 1966). This is of substantial importance in the use of sewage sludge for farm fertilization.

Pleasure boating is an appreciable source of lead contamination of water and about 0.53 g of lead passes into water for each gallon of fuel burned by outboard motors. The 800 million gallons of gasoline burned in recreational motor boats in the U.S. in 1963 thus contributed 400 million grams of lead to restricted aquatic environments.

The average annual deposition of lead from gasoline additives in the United States is of the order of 25 mg/m^2. Since the development of tetraethyl lead in 1923, about 3.10^{12} g of lead has been combusted in the United States (Chow and Johnstone, 1965) for an average contamination of 380 mg per m^2. About half this lead contamination is in large particulate form and should be deposited within a few feet of highways. The 41,000-mile U.S. Interstate Highway System for high-speed driving insures a very wide distribution over the most heavily-settled regions of the United States. Thus the pattern of lead fallout covers about 40 percent of the cropland areas of the United States and averages about 0.04 mg Pb/m^2/day, or in more familiar terms about 0.22 lb/A year (Patterson, 1965). The fact that these figures for lead fallout are realistic is demonstrated by analytical values for lead in roadside vegetation which showed pasture grasses at the intersection of U.S. Highways 6 and 40 near Denver to contain 3000 ppm lead (on a washed dry weight basis). The lead deposits declined with distance from the highway and grass 100 to 1000 feet away contained as much as >10->50 ppm Pb. The distribution of the lead was clearly correlated with traffic volume and prevailing wind currents. Soil pollution along a highway in Canadaigua, N.Y., averaged 515 ppm (100-1000 ppm) (Cannon and Bowles, 1962).

Lead, unlike most other soil pollutants, is almost nonbiodegradable and may be considered to have a soil residence time in excess of 100 years. Thus, for all practical purposes this soil contamination is virtually permanent. In view of the rapidly increasing "lead fallout" this situation deserves immediate study.

Movement of Lead in the Food Chain

The steadily increasing levels of environmental lead pollution discussed above must be reflected in increased lead levels in raw agricultural commodities. Such lead contaminations must affect lead levels in processed foods and beverages. Patterson (1965) has calculated from the fecal excretion of lead, which was 232 μg Pb/person/day in one U.S. urban survey and 398 μg Pb in another (Kehoe, 1961), that the average value represents a lead intake of about 0.17 ppm in food. This value is in agreement with an average of 0.2 ppm suggested by Lewis (1966). This general level of lead pollution in food is reflected in the average values found in U.S. surveys as given in Table 8.

Table 8

Summary of lead pollution of foods

	Lead in ppm		
	U.K.[1]	U.S.[2]	U.S.[3]
Beverages	4.2	0.18	0.05
Cereals	0.5	0.4	0.4
Fruits	0.4	0.5	0.2
Meats	1.5	0.3	0.2
Milk	0.3	0.03	0.2
Vegetables	0.3		0.2
Fish	0.9		0.5
Spices	3.4		0.3

[1] Monier-Williams (1938)

[2] Kehoe (1961)

[3] Schroeder and Balassa (1961)

Milk is of particular interest because of its unique role as food for children and the greater susceptibility of the young to plumbism. There is evidence that "the level of lead in milk is a function of the body burden of the element rather than that in the daily diet." If this be so, then the lead concentration in milk should reflect an "integrated exposure of the cow to lead through her food chain" (Lewis, 1966). Milk levels should serve as a useful indicator of changes in environmental exposure of man to lead. Unfortunately, adequate baseline data are lacking; but data from recent surveys, showing 0.04 ± 0.017 and 0.05 ± 0.025 ppm Pb in market samples, suggest that Pb levels in milk may be slightly higher than 20 to 30 years ago (Lewis, 1966). Critical study of raw milk from cattle fed graze or hay in regions of high lead fallout is apparently lacking and appears to be urgently needed.

The contamination of soil by lead is related to lead uptake in growing plants, and crops grown in soil with high lead content may have as much as 10 times the general content of lead as plants growing in soil with low lead content. Since Cannon and Bowles (1962) recorded lead in soil along a highway near Canandigua, N.Y., as containing 100-1000 ppm Pb (average 515 ppm), this factor is becoming increasingly important.

Contamination of fruits and vegetables grown near areas of high traffic density by lead from exhausts is substantial. Cannon and Bowles (1962) record the following pollution of vegetables in Washington County, Maryland:

Feet from road	Mean Pb content in ash (ppm)
1 - 25	80 (10-500)
25 - 50	66 (10-700)
50 -100	45 (<10-150)
>500	20 (<10-200)

The extent to which such high lead pollution--particularly with soluble $PbCl \cdot Br$--is reflected in increased lead content in finished food products, needs substantial investigation.

Ecological Effects of Lead

There is an astonishing dearth of information on the effects of the environmental distribution of lead upon the growth, development, and behavior of plants and animals and upon various ecological food chains. The virtual ignorance as to the detailed environmental fate of lead provides few clues as to areas where abnormal ecological lesions might be expected. It seems logical to expect considerable concentration of lead in estuaries and lakes collecting freshwater runoff from urban areas where lead deposits have been shown to be concentrated. It is imperative to obtain data on lead concentration in these areas (e.g., Lake Michigan and Lake Erie, San Francisco and Long Beach Bays, etc.) in order to measure the accumulative effects of lead runoff from air pollution. A recent study of lead levels in the bottom sediments of Lake Michigan (Shimp, Leland, White, 1970) has shown substantial accumulations of lead in the upper 2 cm of sediment which, 12 miles east of Waukegan, contained 90 ppm lead as compared with 18-20 ppm in lower levels.

The effects of lead in solution in water upon a variety of organisms have been summarized by McKee and Wolf (1963). *Plants* may be susceptible to lead under a variety of conditions (Klintworth, 1952) and lead salts in irrigation water may be toxic to plants. Lead at 50 ppm killed oats and potatoes in water culture and was injurious to sugar beets. Germination of watercress and mustard seeds was delayed and growth retarded by lead concentrations of 345-1380 ppm.

Plankton are apparently highly sensitive to lead as lead chloride at 0.01-1.0 ppm killed *Daphnia magna* within 10 days. The toxic concentration of lead to flagellates and infusoria is reported to 0.5 ppm. Bacteria are affected by lead at 0.1-1.0 ppm (McKee and Wolf, 1963). Bringmann and Kuhn (1959) found the threshold toxic concentrations for lead nitrate at pH 7.5 over a 4-day exposure to be: *Microreoma* 1.25, *Escherichia coli* 1.3, *Scendesmus* 2.5, and *Daphia magna* 5.0 ppm.

Fish response to lead has been more extensively studied than other aquatic organisms and McKee and Wolf (1963) review a variety of reports that fish--including stickelbacks, guppy, minnow, brown trout, coho salmon--were killed by lead in water at 0.1-1.0 ppm. The median period of survival of rainbow trout in soft water containing dissolved lead was 18-24 hours at 1.6 ppm and 10-12 hours at 4.0 ppm. Death of fish from lead in solution has been reported as due to suffocation from a film of mucous foaming over the gills as a result of reaction with lead. Weir and Hine (1970) have shown behavioral responses in goldfish exposed to lead nitrate at concentrations as low as 0.04 ppm.

Birds. One example of the drastic effects of lead pollution on wildlife has been well investigated and documented, i.e., the lead poisoning of waterfowl from the ingestion of spent shot. Bellrose (1959) has summarized the results of more than 60 years of investigation of lead poisoning in waterfowl and reported that, in the 20 years of 1938-1957, 39 important die-offs occurred involving from 0.145-33 percent of the birds present in the areas investigated in 16 states and killing an estimated 115,000 mallards, pintails, redhead, and green-winged teal, Canada geese, blue geese, snow geese, and whistling sawns. These epidemics of lead poisoning are related to the density of spent shot, the shot size, the firmness and depth of bottom, and the ice cover. Sampling lakes and marshes showed deposition of shot ranging from a few thousand per acre to 100,000 per acre (2.71 per sq. ft.) in Lake Puckaway, Wisconsin. Biological data on 5148 trapped and fluoroscoped mallards showed that 10.14 percent of the birds had shot in their gizzards, and examination of the gizzards of 36,145 waterfowl from 1938-1953 showed shot in 76.8 percent. Experiments indicated that a single No. 6 lead pellet caused an increase in mortality of 9 percent, 2 pellets 23 percent, 4 pellets 36 percent, and 6 pellets about 50 percent. Birds ingesting a single pellet were 1.5 times as vulnerable, and with 2 pellets 1.9 times as vulnerable to hunters as normal birds. The weakness and fatigue caused by lead poisoning affected the migratory habits and behavior of the game birds. From this exhaustive study, Bellrose concluded that "for all waterfowl species in North America, the annual loss due to lead poisoning is estimated to be between 2 and 3 percent of the population."

Mammals. Sanderson and Thomas (1961) studied the incidence of lead in the livers of Illinois racoons and found 1 to 32 µg per gram in 100 individuals. Only one liver was negative, but there were no obvious signs of lead intoxication. There was a seasonal difference in lead levels and evidence of transfer of lead from mothers to offspring in milk or through the placenta. It was concluded "Racoons appear to be resistant to high levels of lead, but in spite of widely varying responses, lead intoxication, along with other factors, may be a cause of mortality in wild racoons."

The fragmentary evidence available indicates that plant and animal life of every description may be susceptible to poisoning, particularly by dissolved lead salts in water. The lethal concentrations to plankton, fish, and other aquatic organisms may range from 0.01-10 ppm, depending upon the duration of exposure and the hardness of the water. There appears to be no thorough study of the effects of lead at subtoxic levels on animal growth, reproduction, or behavior, or upon the possible entrance of lead residues into food chains or the concentrations of lead through ecological magnification. In view of the very high concentrations of lead found on plants near highways, and in rain water and urban runoff, it seems imperative to begin careful long-term investigations of the effects of lead on a representative variety of plant and animal components of various ecosystems.

Public health significance of lead pollution

Lead poisoning, or plumbism, was known to Greek, Roman and Arabian physicians before the Christian era; and its intestinal and neurological manifestations were discussed by Dioscorides in the First Century AD (Cantarow and Trumper, 1944). Lead poisoning is presently important enough to receive an individual heading in the Encyclopedia Britannica. It is described as usually chronic in nature, affecting the entire body, but especially the neuromuscular system where it may cause gradual paralysis, the gastrointestinal tract, the blood-forming organs, and the gonads. It generally results from the cumulative toxic effects of lead ingestion after continuous consumption over long periods of time. In humans, lead poisoning has occurred through drinking water containing 0.042 to 1.0 ppm lead, or through ingestion of 0.1 mg or more daily over a period of years (McKee and Wolf, 1963).

During the seventeenth and eighteenth centuries, outbreaks of lead poisoning occurred throughout Western Europe from the widespread use of lead to promote fermentation of wine, to manufacture and store cider, and for fabrication of cooking vessels and other household articles. Lead poisoning was frequently encountered in young children following the ingestion of lead-containing paints of furniture or toys and was often manifested by severe cerebral involvement or "lead encephalopathy."

The industrial revolution resulted in a tremendous increase in the utilization of lead in pigments, type, cables, solder, batteries, shot, etc., and consumption in the United States has increased from about 540 million pounds in 1900 to 5.99 billion pounds in 1966 (*Minerals Yearbook*). As a result, most industries use lead in some form and the majority of industrial workers are exposed to lead.

The relation of occupational exposure to lead in the battery and gasoline additives industries to plumbism has been intensively studied for more than forty years (Kehoe, 1961) and has resulted in the firm conclusion that "somewhat less than 10 percent of the quantity of lead ingested under ordinary circumstances is absorbed daily from the alimentary tract, while from 20 to 50 percent of that inhaled, dependent upon the size, shape, and density of particles inhaled, is retained and absorbed in the respiratory system." The average quantity absorbed daily in the alimentary tract of the adult is of the order of 30 μg, while a reasonably satisfactory estimate of that absorbed in the respiratory system would not be far from 20 μg (Kehoe, 1966).

This chronic exposure to lead is related to a mean human blood level of 0.25 ppm of lead for the U.S. population (range 0.05-0.4 ppm) (Patterson, 1965), while the lowest blood level related to lead poisoning is 0.8 ppm (Kehoe, 1966). The lack of significant disparity in these two sets of values representing the current biological normal for the healthy and the threshold level for the poisoned has given rise to two viewpoints: The industrial toxicologist maintains (Kehoe, 1966) "In the analytical sense there is a small margin between the upper limit of the concentration of lead in the whole blood of persons in the general population (who have not sustained any unusual exposure to lead) (0.5 ppm), and the lowermost limit of concentration which, occasionally may be associated with the onset of (mild) lead intoxication. In the physiological sense, however, if the accuracy of the analytical findings can be substantiated, the difference is not slight, for many months of potentially hazardous occupational (or experimental) exposure to lead are required to elevate the concentration of lead in the blood by an increment of 0.2 ppm." Thus it has been concluded that existing lead states in the U.S. are "well within the presently-accepted range of lead levels for humans and are not significant in terms of a threat of the occurrence of lead intoxication" (U.S.P.H.S., 1965).

From the geochemical approach, however, Patterson (1965) relates the present average human body burden of lead--200 mg lead for a 70 kg adult (range 90-750 mg), to a carefully estimated natural level (based on the geological distribution of lead) of 2 mg Pb/70 kg man and states "there are definite indications that the residents of the United States today are undergoing severe chronic lead insult. The average American ingests some 400 μg of lead per day in food, air and water--a process which has been viewed with complacency for decades. Geochemical relationships and material balance considerations show that his ingestion of about 20 tons of lead per year on a national basis is grossly excessive compared to natural conditions." In the Soviet Union, Guseuv (1960) has reported that rats exposed to atmospheric concentrations of lead (10 $\mu g/m^3$), corresponding to those present in most large U.S. cities, experienced pathological and histological changes of the brain and spinal cord, bone lead contents of 10 times that of controls, together with functional shifts in higher nervous activity, such as disturbances of conditioned reflexes.

From autopsies of 150 accidental deaths, Schroeder and Tipton (1968) determined that lead concentrations in ribs are accumulated with age from less than 1 ppm at 0-1 year to 43.5 ppm at 30-39 and decreasing slightly with older age. The U.S. adult had a concentration substantially greater than in any other part of the world except Hong-Kong, and it was concluded that the lead exposure in the U.S. from 1952-57 exceeded the ability of the human body to excrete all the lead absorbed.

Lead poisoning in underprivileged urban children has become very widespread, as shown by the statistics in Table 9.

Table 9

Incidence of lead poisoning in children in New York and Chicago

Elwyn, D. (1968)

	Chicago		New York	
Year	Total Cases	Deaths	Total Cases	Deaths
1957	24	7	85	9
1958	13	3	116	21
1959	193	19	171	12
1960	172	28	146	18
1961	178	15	181	6
1962	154	21	198	9
1963	203	19	338	7
1964	156	8	509	7
1965	218	18		
1966	304	5		

Most authorities attribute this disease syndrome in children of up to six years of age as the result of pica, a habitual purposeful ingestion of unnatural food substances. As a result, substantial amounts of lead are consumed from old coatings of lead-based paint used in interior surfaces. Clinical lead poisoning in children may cause colic and general malaise, neuromuscular impairsments, encephalopathy, and death. Subclinical manifestations can result in destruction of red blood cells, reduction in hemoglobin formation, mitochrondrial morphologic changes and ribosomal abnormalities, and injurious effects on germ cells. Elevated blood levels have been found in 5 to 10 percent of children in a number of municipalities (USPHS, 1970) and blood lead levels as low as 5-10 μg per 100 ml blood have been shown to reduce the activity of the enzyme delta-aminolev linic acid dehydrogenase in the erythrocytes.

In addition to the hazards of ingestion of paint, the child's body burden of lead is enchanced by inhalation of airborne lead particles, eating food contaminated with lead, and drinking from pottery and other utensils containing leachable or extractable lead. All of these sources are contributory to both chronic and epidemic lead poisoning in the urban environment. The incidence of lead poisoning markedly increases in the summer, with from 45-85 percent of the reported cases occurring from June through September. Both, physiological factors--such as increased vitamin D production from sunlight, which influences mineral metabolism --and environmental factors--such as increased outdoor exposure to lead aerosols and surface coatings--have been suggested as causative (USPHS, 1970).

It may be concluded, therefore, that we are dealing with a problem of public health significance lying between two extremes: (a) a problem of environmental quality of largely unexplored dimensions whose potentially serious nature is steadily increasing as the tonnage of atmospherically-dispersed lead aerosols grows at the rate of about 5 per cent per year (see Figure 1); or (b) a problem involving the total environmental exposure of all living organisms to an extremely persistent and highly toxic element which even at levels below those causing symptoms of chronic poisoning may produce insidious effects on blood, nerve and genetic tissue which may affect growth, reproduction, life span, and mental processes. Within this area of uncertainty there appears to be an urgent need for the establishment of the allowable limits of environmental pollution before the point of no return.

Mercury as an environmental pollutant

Mercury, because of its liquid nature, occupies a unique place as an industrial metal. Since 1900 more than 200 million pounds have been used in the United States and it has been estimated that as much as one-third has been "lost" to the environment (Hammond, 1971). In 1968 the United States utilized about 30 percent of the world's production. A summary of industrial utilization in the United States is presented in Table 10.

Table 10

Industrial Consumption of Mercury in the United States

U. S. Bureau of Mines, Minerals Yearbooks

	Thousand Pounds					
	1963	1964	1965	1966	1967	1969
Electrolysis; chlorine, soda	608	728	665	877	1090	1572
Electrical apparatus	846	812	1060	1001	1050	1382
Industrial instruments	375	378	351	311	294	391
Redistilled	700	887	923	552	556	---
Laboratory use	385	1340	85	119	86	126
Fungicides, bacteriocides	193	239	236	179	283	204
Pharmaceuticals	310	383	248	279	148	52
Dental	178	198	123	101	103	209
Paints - antifouling, antimildew	506	414	590	600	479	739
Paper manufacturer	215	163	47	46	34	42
Miscellaneous	1539	640	1260	1354	1160	1097
TOTAL	5720	6160	5590	5440	5280	6035

The principal use of mercury has been as a cathode in the electrolytic preparation of chlorine and sodium hydroxide; electrolytic processes currently supply 30 percent of the U.S. supply of chlorine. Small but regular losses of mercury occur during the operation of the electrolytic cells and approximately 287 lbs. of mercury a day were being lost directly to the aquatic environment as Hq^0 and Hg^{2+} in July 1970. The total replacement of mercury required in this industry was 1,300,000 lbs. per year in 1968. Significant losses of Hg metal to the environment also occur from the electrical industry, especially in the disposal of used mercury alkali batteries which contain 8 percent Hg. Mercury, because of its fluidity, high specific gravity, and electrical conductivity, is essential in electrical control apparatus and significant amounts of Hg^0 are lost here as they are from general laboratory use and from disposal of broken thermometers. Mercury is used as a catalyst in the manufacture of acetaldehyde and vinyl chloride and the effluents from these processes have caused severe environmental pollution in Japan.

The most direct and potentially dangerous dissipation of mercury into the environment occurs from the widespread use of organomercurial compounds as fungicides, bacteriocides, pharmaceuticals, and anti-foulng and mildew-proofing paints. The agricultural use of methyl- and methoxyethylmercury fungicides (CH_3Hg^+ and $CH_3OCH_2CH_2Hg^+$) as seed dressings has been widespread and has resulted in a general contamination of terrestrial animals in every country where they have been used. Wild game throughout Western United States and Canada are contaminated with mercury from this source, reaching 2.3 ppm in North Dakota ducks (Eyl, 1971). More than 42 individual organomercury compounds have been sold in the U.S. for these purposes. Treated grain used directly for animal and human consumption has caused disastrous epidemics of mercury poisoning. Phenyl mercury compounds ($C_6H_5 \cdot Hg^+$) were used widely for many years as slimicides in the paper and pulp industry with direct release into rivers and lakes. The total deliberate environmental application of organomercurials in the United States in 1969 was about 943,000 lbs. In addition mercury has had a widespread, although declining, use in medicine for antacids, astringents, eye-drops, laxatives, nasal sprays, skin antiseptics, contraceptives, douches and suppositories. More than 160 products of this kind carry mercury directly into sewage. Mercury compounds are formulated into cosmetic products such as creams, lotions, hair preparations, and make-up for over-counter sale (Wallace *et al.*, 1971).

The mercury biocides are almost exclusively alkyl, alkoxy, or phenylmercury derivatives which, unlike inorganic mercury salts, are lipid soluble and exhibit passage through food chains and ecological magnification. For example, the bald eagle in Minnesota has been reported to contain 117 ppm mercury, and 25-170 ppm have been found in the livers of fur seals and sea lions in estuarian sites in Western North America (Wallace *et al.*, 1971). These compounds also readily pass placental and blood brain barriers in animals, including man.

The widespread use of mercury in dental amalgrams is believed to have no adverse effect on the user, although the disposition of waste products is uncertain. Other major sources of mercury contributing to environmental pollution include: erosion from mine tailings, the combustion of fossil fuels, and smelting of ores. U.S. coals contain from 0.5 to 3.3 ppm mercury, and the annual combustion of 550 million tons could release from 550,000 to 3,600,000 lbs. of mercury. The smelting of tin, zinc, copper and gold ores releases substantial amounts of mercury impurities which are largely emitted as Hg^0 vapor (Wallace *et al.*, 1971).

As a result of the widespread industrial use of mercury, as with lead, the contamination of the biosphere with mercury is steadily increasing. This is dramatically shown by increasing levels of mercury found in the feathers of crested grebes and goshawk in Sweden during the period 1840-1965 (Johnels and Westermark, 1969).

Period	ppm in feathers grebe	 goshawk
1840-1964	---	2.5
1865-1889	5.2	1.0
1890-1914	7	2.5
1915-1939	10	2.4
1940-1965	18	20.3

Ecological effects of Mercury

The widespread distribution of mercury in the biosphere and the lipid solubility of organomercury compounds has resulted in grave environmental insults to wildlife populations. In the United States these went almost unnoticed until the dramatic revelations of the extent of mercury pollution of game fish during the summer of 1970 (*Chemical and Engineering News, 1970*). However, in Japan and Sweden, pollution of aquatic life had been observed since 1964. The experience in Sweden with the widespread use of mercury seed dressings and contamination of estuaries from industrial effluents has been reported by Johnels *et al.*, (1967) who had found an overall concentration of methylmercury from water to predaceous fresh-water pike Esox lucius (9.8 ppm in muscle) of about 3000-fold. There was a direct relationship between the weight (and age) of the pike and the body burden of Hg.

Surveys of fish from Lake Erie and the St. Clair Rivers, both substantially contaminated with mercury effluents from chlorine plants, have shown high levels of contamination (*Chemical and Engineering News, 1970*) as shown in Table 11.

Table 11

Mercury levels in fresh water from Lake Erie and St. Clair River

Chemical and Engineering News (1970)

Fish	Mercury ppm - wet weight
Walleye pike	1.40 - 3.59
Sucker	0.88
Northern pike	0.64
White bass	0.53 - 0.80
Channel catfish	0.32 - 1.8
Yellow perch	0.34 - 1.7
Coho salmon	0.24 - 0.96
Gizzard shod	0.24
Sheepshead	0.24
Steelhead	<0.15
Carp	0.08 - 0.28

As a result of this sort of information, restrictions have been placed on sport and commercial fishing in more than 18 states and the very existence of a $500,000,000 industry is threatened.

Fish can accumulate methylmercury from bottom sediments either through food chains or directly from the water. The extent of accumulation depends on length of exposure, age, size and species. There appears to be a linear relationship between age or weight of fish and accumulation of methylmercury in muscle once the threshold level (>0.2 ppm), below which elimination is rapid, is exceeded (Lofroth and Johnels *et al.*, 1969). Weir and Hine, (1970) have shown behavioral impairment in goldfish exposed to mercuric salts at concentrations as low as 0.003 ppm.

The high levels of accumulation of mercury which can occur in wildlife such as the bald eagle (117 ppm) and the lievers of fur seals and sea-lions (25-170 ppm) has been mentioned above. A comprehensive survey of mercury levels in Canadian fish and birds has shown the almost ubiquitous distribution of this pollutant at levels ranging from 0.004 to 0.460 ppm in pheasants, 0.08 to 1.54 ppm in walleyed-pike, and averaging 0.22 ppm in halibut, 0.17 ppm in mackerel, 0.05 ppm in cod, 0.12 ppm in flounder, 0.16 ppm in crab, 0.01 ppm in scallops, and 0.068 ppm in oysters. In the United States, pheasants contained up to 4.7 ppm., shoveler ducks 0.17-2.26 ppm, and walleye-pike 0.5-3.6 ppm (Wallace *et al.*, 1971).

Methylmercury and Hg^0 can also accumulate to very high levels in a variety of aquatic invertebrate organisms. Johnels and Westermark (1969) have documented the accumulation of mercury from the effluent of a paper mill as shown in Table 12. Such accumulations can obviously be passed along to organisms such as fish, raptorial birds, and man in the upper trophic levels.

The very widespread use of organomercual seed dressings to protect developing seedlngs from fungal and bacterial infection has occasioned severe environmental pollution problems not only on birds and other wildlife, which consume seeds prior to germination, as mentioned above, but also through persistence of methylmercury through the plant food chain. Such seed dressings were in widespread use in Sweden from 1940 to 1966, with especial usage of Panogen ^{R} , methylmercury dicyandiamide, at 1.6 g per 100 kg of grain. Harvested barley and oats from treated seed were found to contain about 0.03 ppm Hg as compared to 0.014 ppm in untreated seed (Lagervall and Westöö, 1969), and the average mercury content of hens eggs fed grain grown from treated seeds was 0.027 ppm as compared to 0.012 ppm from untreated seed (Westöö, 1969) During 1964-65 it was demonstrated that Swedish eggs were widely contaminated with mercury to an average of 0.029 ppm as compared with a level of 0.007 in eggs from 6 countries of Continental Europe where Panogen ^{R} was not widely used. The levels in Swedish eggs were such that daily consumption of two eggs could mean an intake of mercury above the FAO/WHO safe level of mercury intake 0.00005 mg Hg/bg body weight. In the ensuing furore, alkyl-mercury seed dressings were banned in Sweden on February 1, 1966, and the mercury levels in Swedish eggs (96 percent methylmercury) decreased from an average of 0.029 ppm in April 1966 to 0.019 by November 1966, and to 0.010 by September 1967 (Löfroth, 1969).

Table 12

Accumulation of mercury by invertebrate organisms
on stream below paper mill

Johnels and Westermark (1969)

Organism	Location on stream	Mercury-ppm
Hirudinia (leech)	Above mill	0.02
	Below mill	2.6 -4.4
Asellus (isopod)	1 km. above mill	0.06
	20 km. below mill	1.9
Trichoptera (caddis fly larva)	14 km. above mill	0.05
	1 km. below mill	17.0
	5 km. below mill	5.6
	6 km. below mill	10.7
Plecoptera (stone fly larva)	15 km. above mill	0.07
	17 km. below mill	2.40
Sialis (alder fly larva)	1 km. above mill	0.05
	1 km. below mill	5.50
	6 km. below mill	4.80

The use of mercury seed dressings in Sweden was shown to result in lethal levels of mercury, 4-200 ppm, in the livers and kidneys of seed-eating birds. Rodents eating such seeds, and their predatory foxes, contained up to 2 ppm mercury as compared with mercury levels of 0.006 to 0.055 ppm in true herbivors (Wallace *et al.*, 1971). It was concluded, after much study, that large numbers of seed-eating animals showed symptoms of mercury intoxication. The consumption of mercury-treated seeds by humans represents the most telling example of the environmental hazards of mercury pollution. In 1960 in Iraq several hundred human cases of poisoning from this source occurred, with many deaths. The average mercury content of the livers of the victims was 65.8 ± 18.5 ppm. The fungicide responsible was Granosan-M^{R} containing ehtylmercury-p-toluenesulfonanilide and symptoms of poisoning occurred from a few days to two months after consumption of the treated grain. In 1969, in the

United States, a custodian in a granary collected about 3000 lbs. of floor sweepings of grain treated with Panogen ^{R} to feed to his hogs. A number of the animals appeared sick after about three weeks, and one was butchered and fed to the family. After about three months three of his children developed impaired vision and became comatose. Hair samples contained 1,397 and 2,436 ppm mercury, and the children were still critically ill after six months.

Allowable daily intake

Scanty data exists to evaluate the allowable daily intake of mercury. The FAO/WHO standard for phenylmercury is 0.003 mg per day. Studies with methylmercury-contaiminated fish in Sweden suggest an ADI level of 0.1 mg per day for methylmercury--and this agrees with metabolism studies with radio-labeled methylmercury based on retention levels which suggest an ADI level of 0.06-0.12 mg per day (Löfroth, 1969).

Mercury poisoning in man

The syndrome of mercury poisoning has been recognized since the Middle Ages and is exemplified by the classical picture of the "Mad Hatter." The symptoms of human poisoning are: 1) excessive weakness, fatigue, apathy, lack of interest; 2) paresthesias of perioral area and the extremities; 3) tunnel vision, hearing difficulties, fits of rage and depression; 4) dysarthria, dysdiadochokinesia, atoxia, alexia, agraphia, clumsiness, intention tremor; and 5) gross motor incoordination, spasticity, paralysis, coma, and death (Eyl, 1970). These have been repeatedly observed in persons exposed from industrial accidents, such as hat-felt workers exposed to air mercury levels of 100 $\mu g/m^3$ and chloralkali workers. Experience in the USSR indicated that hyperexcitability of the central and autonomic nervous system can occur following exposure of workers to 10-30 $\mu g/cm^3$. Airborne mercury effluents from a fire in a mercury mine in Yogoslavia produced typical symptoms of intoxication in a community of 900 inhabitants along with their domestic animals (Wallace *et al.*, 1971).

The most insidious cases of human poisoning have resulted from ingestion of food contaminated with mercurial seed dressings, as mentioned above, or from eating seafood contaminated with mercury. The episodes of Minamata disease in Japan are most instructive. In the area around Minamata Bay, an acetaldehyde and vinyl chloride plant discharged large amounts of mercuric chloride and methylmercury. Fish and shellfish from the bay were subsequently found to contain 27-102 ppm mercury and over the period 1953 to 1960, the inhabitants, whose diet was largely seafood, experienced 111 cases of poisoning, with 41 deaths, including 19 congenitally-defective babies born of mothers who had eaten contaminated fish. The tragic incident was repeated in Niigata, Japan, in 1965, where as many as 120 persons may have been affected (Wallace *et al.*, 1971).

Mercury levels in whole blood and red blood cells of fatal Japanese cases of poisoning reached 1300 and 2400 ppb, as compared with 5 to 10 ppb for humans with normal exposure. Levels of mercury in the hair of the victims reached 500 ppb as compared with a normal of 10. These levels compare with blood levels of 52-155 ppb (whole) and 96-287 ppb (red cell) found in inhabitants of Michigan and Ontario, Canada, who had consumed large amounts of fish from Lake Erie (Eyl, 1971).

Added to the dangers of chronic mercury poisoning are reported mutagenic effects of mercury salts and the extreme sensitivity of the fetal nervous system.

Anaerobic methylation of mercury

The seriousness of environmental pollution by inorganic mercury has been heightened by recent discovers that anerobic bacteria such as Methanobacter omelianskii can methylate inorganic mercury to produce dimethylmercury $(CH_3)_2Hg$, b.p. 96°C. (Wood *et al.*, 1968). The dimethylmercury is both volatile and lipophilic and this mechanism provides a normal biological process for the progress conversion of deposits of inorganic mercury in the muds of rivers and lakes to dimethylmercury which can enter into and concentrate in food chains and can readily pollute the air as a vapor. Dimethylmercury is readily converted to methylmercury of acidic pH. The conversion of sinks of metallic mercury is favored by the anaerobic ecosystems which are particularly characteristic of the polluted waters of our industrialized society.

Mercury Standards and Tolerances

Air: No official standard for mercury in air presently exists in the United States. Informal tolerances recommended by the American Conferences on Governmental and Industrial Hygienists are industrial threshhold limits of 100 $\mu g/m^3$ for organic mercury compounds. Sweden has established maximum allowable concentrations of 50 $\mu g/m^3$ for alkylmercury compounds and advised that women of childbearing age should have no exposure to alkylmercurials. In the U.S.S.R., permissible limits have been established as 10 $\mu g/m^3$ for inorganic mercury and 5 $\mu g/m^3$ for alkylmercury compounds (Wallace *et al.*, 1971).

Water: A standard of 5 μg/liter (ppb) has been tentatively established by the U. S. Public Health Service for mercury in drinking water. This is considered to provide a reasonable safety factor for the protection of human health. However, the State of Illinois has established a safe standard of 0.5 ppb mercury for drinking water.

Food: The ubiquitous presence of mercury in animal tissues and in seafoods has caused much concern about safe standards in food. The World Health Organization has recommended that the Average Daily Intake for organic mercurials be zero, and has set the practical limit at 0.02 to 0.05 ppm. The U.S. Food and Drug Administration has set a tentative limit of 0.5 ppm and regulatory action can be taken against any food containing levels in excess of the tentative tolerance. Thus, many freshwater and marine fish--including canned tuna and wild game--contain illegal levels of mercury (see Table 11, page 39).

Cadmium as an environmental pollutant

Cadmium is the latest example of a trace metal which appears to be a serious environmental pollutant. Cadmium is utilized in the United States at the rate of 13,328,000 lbs. per year, or about 43 percent of world production. Its principal uses are shown in Table 13. Cadmium may enter the environment through metallurgical processing, where it is estimated that about 2,100,000 lbs. enter the air yearly (Davis, 1970), by incineration of wastes, as an inpurity in fertilizers, from the application of pigments such as cadmium sulfide and cadmium selenosulfide used to color glass, plastics, and enamels; from barium cadmium stabilizers of polyvinyl chloride plastics; and from disposal of nickel-cadmium batteries. Cadmium fungicides are used at the rate of about 25,000 lbs. per year.

Table 13

Industrial consumption of cadmium in the United States

W. E. Davis (1970)

	Million Pounds 1968
Electroplating	6
Pigments	2.8
Vinyl stabilizers	2
Alloys	1
Batteries	0.4
Fungicides	0.025

A major source of environmental contamination is through cadmium plating of automobiles, aircraft, and machinery. The automobile is an important contributor of cadmium as this metal accompanies zinc in automobile tires in which the latter is used in vulcanization as zinc dimethyldithiocarbamate. Tires contain 20-90 ppm cadmium, and this is emitted at the rate of 11,400 lbs. per year in tire wear. Cadmium has been found as a contaminant of roadside vegetation at 0.5-1.0 ppm and in the adjoining soil at 0.2 to 1.8 ppm (Langerwerff and Sprecht, 1970).

Cadmium and public health

Cadmium is known from industrial exposure to be highly toxic when inhaled by humans, as it is excreted only very slowly. The inhalation of 40 mg and the retention of 4.0 mg in a human has been fatal. It causes liver and kidney damage, gastrointestinal inflammation, cardiovascular disease, and fatty degeneration of the heart and liver. Recent dramatic publicity (Time, 1971) has been given to an industrial worker who inhaled cadmium particles in a Japanese smelter. After prolonged suffering of intestinal pain for nearly 10 years, she committed suicide. At autopsy, her liver contained 4540 ppm and her kidneys contained 22,400 ppm of cadmium. Cadmium inhibits sulfhydryl enzymes in all accessible tissues.

Samples of Japanese wheat and cabbage have been shown to contain 17.8 ppm of cadmium. It now appears that cadmium is a dangerous environmental pollutant that is responsible for a widely-distributed human syndrome called "itai-itai" or "ouch-ouch" disease. Almost nothing is known of the environmental fate of cadmium.

Antimony as an environmental pollutant

The United States uses about 37,000 lbs. of antimony yearly, or about 27 percent of world production. The large variety of its industrial uses, which closely resemble those of lead, are shown in Table 14. Very little information is available about its ecological fate or possible effects on public health. Experience with lead suggests the importance of such studies.

Table 14

Industrial consumption of antimony in the U.S.

U. S. Bureau of Mines, Minerals Yearbooks

			Thousand Pounds		
	1963	1964	1965	1966	1967
Ammunition	12,524	11,904	12,764	12,570	11,078
Metal products	4,668	3,798	4,508	4,302	3,990
Flameproofing chemicals	3,202	3,252	3,942	6,376	6,908
Ceramics	2,930	3,298	3,706	4,148	3,768
Pigments	2,018	2,346	1,710	1,664	1,330
Plastics	2,704	2,578	2,938	4,448	3,570
Rubber products	1,194	984	954	1,740	1,896
Miscellaneous	3,424	3,518	3,316	4,114	2,154
TOTAL	33,064	31,678	33,838	39,362	34,700

Arsenic as an environmental pollutant

The history of the use of arsenic dates back to about 500 B.C. when arsenic derivatives were used medicinally. The Greeks and Romans used arsenical sulfides, As_2S_2 (red) and AS_2S_5 (yellow) as pigments. The use of arsenicals for human poisoning was rather widely practiced in the Middle Ages. The widest deliberate pollution of the environment by arsenic has resulted from the use of paris green, $2\ Cu(AsO_2)_2 \cdot CU(C_2H_3O_2)_2$, lead arsenate $PbHAsO_4$, and calcium arsenate, $Ca_3(AsO_4)_2$, as insecticides. This was widely practiced in the United States from 1921 to 1950 and an estimated 100,000,000 lbs. per year of total arsenicals were applied to such crops as cotton, tobacco, and tree fruits. Sodium arsenite, $NaAsO_2$, and arsenic trioxide, As_2O_3, have been widely used as soil sterilants. As a result of these uses the arsenical contents of some orchard and tobacco soils have increased to 5 ppm or more, and there has been a 300 percent increase in the amount of arsenic in cigarette tobacco grown in treated fields.

Accidental environmental pollution by arsenic occurs through its presence as a trace impurity in phosphate fertilizers and phosphate detergents. The world average contaimination in phosphate rock is 20.9 ppm of arsenic, so that the regular application of phosphate fertilizers makes measurable contributions of arsenic to the soil.

Arsenic is also a contaminant of coals containing pyrites, and it was found in 1933 that English cities had arsenic concentrations of 50-400 ppm in their atmospheres. Arsenical levels of 10-70 ppm occur in detergents and arsenical concentrations in wash waters may reach 5-100 ppb. Thus, the Kansas River has been found to contain arsenic levels of 2-8 ppb (Angino, 1970).

Little is known about the ecological fate of arsenic or the effects of trace pollution on human health. Behavioral impairment has been observed in goldfish exposed to arsenic salts at concentrations as low as 0.1 ppm (Weir and Hine, 1970).

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METHYLATION OF HEAVY METALS

J. M. Wood

In Medieval England, mercury metal (quicksilver) was used as an agent to procure abortion and to commit suicide. In some countries in the Far East small doses of mercury metal are used as a potent diuretic. A perfect example of a person suffering from chronic mercurial poisoning is depicted in "Alice in Wonderland" where we have the charming character of the Mad Hatter. The hatters in Londo would use mercuric oxide in the treatment of velvet, and constant contact with this mercury salt would allow its passage through the skin into the bloodstream. After a number of years the mercury would accumulate to a level where the "hatter" would become a mental defective. The tragedy of the Mat Hatter also applied to some members of the dental profession who succumb to mercury poisoning as a result of constant exposure to mercury vapor when mixing the mercury-silver amalgam for fillings. These two classical examples of mercury poisoning are restricted to symptoms developed due to excessive contact with inorganic mercury (mercury metal or mercury salts) which does not pose a threat to the health and welfare of the general public.

In 1968 we discovered that inorganic mercury is converted to deadly poisonous methylmercury by microorganisms which use methyl-Vitamin B_{12}. This conversion to methylmercury in the environment adds to the methylmercury used as a fungicide in agriculture to pose a serious threat to the health and welfare of the general public. It has now been established that methylmercury is beginning to accumulate in a number of foods common to the diet of U.S. citizens.

Mercury pollution can be conveniently divided into two categories: (1) intentional pollution, and (2) unintentional pollution. Intentional pollution is concerned with the widespread distribution of methylmercury in agriculture, and this represents about 10% of the total mercury used in the U.S.A. Unintentional pollution involves mercury losses in a variety of forms by industry, hospitals, power plants, and institutional research laboratories.

Unintentional Pollution

Industrial chemists did not realize that mercury losses in industrial effluents would lead to the formation of methylmercury by microorganisms to establish a food chain for the accumulation of this deadly poisonous compound in fish. Twenty-six thousand tons of chlorine are manufactured daily in the U.S., and 25% of this chlorine is manufactured by the electrolysis of brine, using mercury metal as an electrode. Consequently significant quantities of mercury metal and mercury salts have been widely distributed in inland and coastal waterways in the U.S. and Canada. To give an example of the extent of mercury losses, 200,000 lbs.

of inorganic mercury has been deposited in the St. Clair River System in the last twenty years. The chlorine industry is not the only negligent body in this respect, since significant quantities of mercury compounds are lost in the following processes:

- Plastics industry - in the manufacture of vinyl chloride. Losses of both mercury salts and a small amount of methylmercury by-product.
- Paper industry - Losses of mercury metal and mercury salts as impurities in the caustic soda used in bleaching. Also, phenylmercuric acetate (PMA) was used as a slimicide by the paper industry. This practice has now been stopped, but significant levels of PMA still pollute waterways owing to the large quanities used.
- Electronics industry - Losses due to the increased use of mercury metal.
- Hospitals - Losses due to the use of mercury salts in histology laboratories.
- Power companies - Losses of mercury metal from coal.
- Institutional research laboratories - Losses due to many varieties of mercury compounds.

The first major incident of methylmercury poisoning, as a result of industrial effluent, occurred in the town of Minamata, Japan. In 1953, it was noticed that cats became terribly ill, screaming incessantly, and some of them committed hari-kari by diving from the cliffs into the ocean. Shortly afterwards a number of fishermen and their families became seriously ill. It was thought initially that this epidemic was caused by an infectious agent (bacteria or virus) which was transmitted from cats to humans, and so this syndrome was called "Minamata Disease". An investigation made by the Japanese Health Authorities established a link between the quantities of fish eaten by afflicted families and their cats. Subsequently, it was discovered that the effluent from a vinyl chloride plant contained high levels of mercury salts and small contaminating levels of methylmercury. When cats were fed on the factory effluent they developed exactly the same symptoms as the cats fed on Minamata Bay fish. Therefore, it was concluded that methylmercury was concentrating through food chains which ultimately led to high concentrations in Minamata Bay fish. However, the vinyl chloride plant at Minamata called in its own expert to investigate "Minamata Disease", and the results of the industry survey indicated that methylmercury could not be the causative agent since fish caught in other coastal areas of Japan contained equally high levels of mercury to those taken from the Minamata Bay area. As a result of the factory study, the Minamata case was closed. Between 1953 and 1960, 116 people were irreversibly poisoned (6 died) by Minamata disease. Irreversible mercury poisoning is defined as the point where brain cell damage is extensive and the victim remains a mental defective for the rest of his life.

In 1965 a second incident occurred at the coastal town of Niigata. Once again a vinyl chloride plant was implicated. Cats committed hari-kari, and 120 people were affected (26 irreversibly and 5 died). It was established that mercury levels were high in the factory effluent, and a connection between fish location, consumption and affliction was established. Further scrutiny of the Minamata factory report to the Japanese health authorities revealed that for their survey of methyl mercury levels in fish they had only analyzed fish caught close to vinyl chloride and chlorine plants. Therefore, the industrial report was not exactly honest.

More recently (1970) a number of fishermen in the town of Ravenna on the east coast of Italy were seriously affected after consuming fish taken near a chlorine plant. This year (1970) U.S. waterways in 17 states have been shown to contain elevated levels of methylmercury, and many areas have been closed to fishing indefinitely. The Department of Justice is taking legal action against over 40 factories in the U.S. for indiscriminate dumping of mercury. A good illustration of the impact of industrial pollution of the St. Clair River System is the observation that the mercury concentration in fish caught in Lake St. Clair in 1935 gives 0.07 to 0.11 ppm. These data are to be compared with fish taken from the same area in 1970 which have 7.0 ppm. During this 35-year period of industrial growth as much as 100-fold increase in the methylmercury levels in fish has occurred, rendering them totally unfit for human consumption. Our inland and coastal waterways are so polluted that elevated levels of mercury are found in tuna and swordfish (although the industrial practice of deepsea dumping of wastes may have contributed greatly to this problem).

Since industrial pollution largely concerns inorganic mercury, and since methylmercury is the compound which accumulates in fish, then, clearly, this methylation reaction occurs in the environment. In 1966 my research group considered which biological methylating agents could yield methylmercury, and in 1967 we discovered that methyl-vitamin B_{12} would perform this reaction. In 1968 we published our results in Nature, and we issued a warning of the dangers of extensive mercury losses to the environment. The formation of methylmercury is accomplished by microorganisms which live in both the presence and absence of air. Some dimethyl mercury is synthesized, and this is volatile so it is dispersed in the atmosphere, coming down with rainfall to pollute rivers and lakes a significant distance away from areas of major pollution.

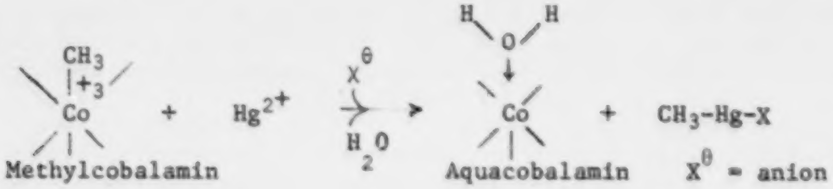
Methanogenic bacteria form an integral part of any sludge ecosystem. These microorganisms utilize H_2 gas as an electron donor and CO_2 as electron acceptor in the following general reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O.$$

The final methyl-transfer reaction in methane formation involves the coenzyme methylcobalamin (methyl-B_{12}). Mercuric salts have been shown to inhibit methane formation in extracts of the methane bacterium M.O.H.

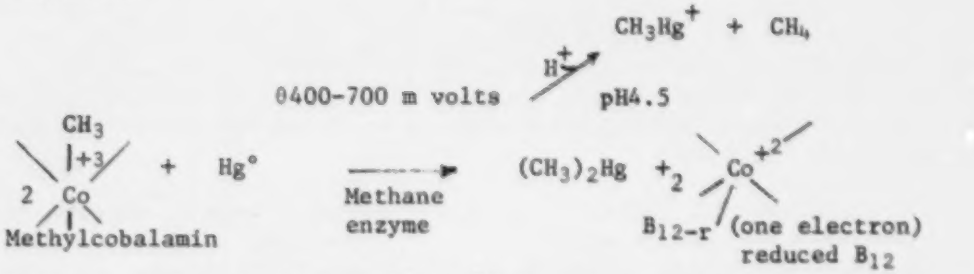
Depending on the concentration of Hg^{2+} added, methyl groups are transferred to mercury to give dimethyl mercury and monomethylmercury. These methyl-transfer reactions can be divided into two alternative mechanisms:

(a) non-enzymatic


CH3
+3
Co
Methylcobalamin
+
Hg2+
Xθ
H2O
H
O
H
Co
Aquacobalamin
+
CH3-Hg-X
Xθ = anion

This reaction occurs in the absence of enzyme and in the absence of reducing conditions. The methyl group is transferred as an anion from Co^{+3} to Hg^{+2}. Since methylcobalamin is a common coenzyme in both anaerobic and aerobic bacteria, significant quantities of methyl-B_{12} derivatives are present in sludge promoting this chemical methyl transfer.

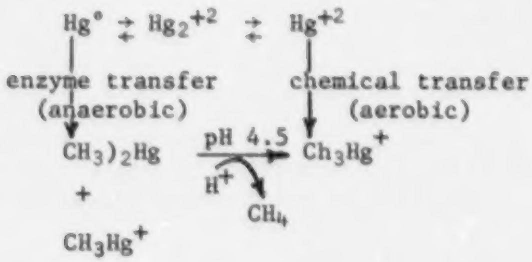
(b) enzymatic


CH3Hg+
+
CH4
H+
0400-700 m volts
pH4.5
CH3
+3
2 Co
Methylcobalamin
+
Hg°
Methane enzyme
(CH3)2Hg
+2
Co
+2
B12-r (one electron) reduced B12

Under anaerobic conditions the Hg^{2+} is reduced to Hg°, and depending on the concentrations of Hg° dimethyl and monomethyl mercury are formed as products. In this reaction evidence is available to support that the methyl group is transferred as a radical.

The results summarized in this introduction are those obtained in the laboratories of Williams and his research group at Oxford University, England, and our own research group at Illinois.

Since inorganic forms of mercury equilibrate in the environment, then the synthesis of methyl mercury compounds can be summarized as follows:


Hg°
Hg2+2
Hg+2
enzyme transfer
(anaerobic)
chemical transfer
(aerobic)
CH3)2Hg
+
CH3Hg+
pH 4.5
H+
CH4
Ch3Hg+

Once methylmercury has been synthesized by bacteria it can enter food-chains through phytoplankton to fish. Clearly the biological activity in the sediments of a mercury-polluted area determines the rate of methylmercury formation, which in turn dictates the extent of methylmercury pollution in fish. Fish accumulate methylmercury because they metabolize it very slowly. The biological half-life for methylmercury in fish is 500 days in summer months and 3 years in winter months. The nature of the complex formed between methylmercury and fish protein is not yet known. However, it must be a very stable complex since boiling, frying, freeze-drying, and drying at high temperature will not remove any methylmercury from the protein.

Intentional Pollution

In 1950 it was recognized in Sweden that a number of seed-eating birds, carrion, and predatory birds suffered from severe poisoning. These poisoning cases were ultimately traced to the use of methylmercury in seed treatment. Methylmercury is very effective for the prevention of fungus rot in planted seeds. Severe poisoning of Swedith birds over a period of 10 to 15 years caused the Swedish Plant Protection Agency to recommend that the use of methylmercury in agriculture be cut in half. In the Fall of 1965 bird populations still continued to be hard hit by methylmercury poisoning, and increased methylmercury concentrations were found in Swedish agricultural products (particularly eggs). In February (1966) legislation was passed against the use of methylmercury in Swedish agriculture.

At the time of this legislation 2 metric tons/year of methylmercury was distributed in Sweden compared to 400 metric tons used in the U.S. in 1966. From 1966 to 1968 the use of methylmercury in the U.S. increased to 750 metric tons/annum. This increase in the use of methylmercury compounds in agriculture caused the hunting season for pheasant and Hungarian partridge to be cancelled in Alberta in 1969, and elevated methylmercury levels have been reported in California, Montana and Ohio. In 1970, judges in Chicago and Washington overturned restrictions placed by USDA on the further distribution of these deadly compounds. The basis for the two judges to support continued use of methylmercury was that the only recorded human fatalities came as the result of improper usage of these fungicides. It is true that the levels of methylmercury compounds applied to date have not yet had time to enter sufficient food-chains to wipe out the human race. But how long will it be before this happens?

Analytical Methods

A variety of analytical methods have been used to determine total mercury concentrations in foods, water, and tissues. Many of the methods that are used suffer from serious defects, since analytical chemists have not recognized that methylmercury is the dangerous poison, and it is this compound which represents 95-100% of accumulated total mercury in foods.

Flameless atomic absorption analysis is the most popular method used by FDA, FWQA and USDA. This method is accurate for inorganic mercury, but for methylmercury analysis it can be as much as 100% low. Neutron activation analysis has proved to be the most reliable method available at this time, but it is seldom used because it is time-consuming and expensive. It is difficult for me to understand why time should be given preference over accuracy when the health and welfare of the general public is concerned!!!

Finally, it should be recognized that volatile alkylmercury compounds may be present in all biological materials subjected to analysis. Methyl mercury, thiomethyl (CH_3-Hg-S-CH_3) and dimethyl mercury $(CH_3)_2$ Hg would easily be lost in both atomic absorption and neutron activation analysis preparative procedures. This special problem should be of concern to scientists working in the area of total mercury analysis.

Possible Solutions

Large quantities of mercury in various forms have been deposited in our environment. Only a small percentage of the total mercury deposited has been converted to methylmercury by microorganisms. For example, in the St. Clair River System it is estimated that the total concentration of mercury in the total fish population is approximately 100 lbs. Since 200,000 lbs. of mercury have been deposited in that area it is clear that the mercury pollution problem has only just started. If 95% of this mercury could be removed from the sediments in this system it will still take many years before fish will be fit for human consumption in this area.

We face two alternative situations: (1) Find a good way to remove mercury compounds from sediments, or (2) find a good method to remove methylmercury from fish protein. Possible procedures for removing mercury compounds from sludge are presented in:

(a) Dredging

(b) Covering the polluted sediments, and creating a new layer of biological activity.

(c) Slowing down the formation of methyl-Vitamin B_{12} by microorganisms. This would slow down the rate of formation of methylmercury to a point where it is equal to or less than the rate of methylmercury metabolism in fish.

Any or all of these three approaches may be used, depending on the specific conditions of the lake or river being considered. A concentration of 0.3 ppm for mercury in sediments does not appear to cause significant increases for methylmercury in fish. Sediments which contain greater than 0.3 ppm should be dealt with in the near future. Fortunately, methylmercury has a biological half-life in humans of 70 to 74 days, but as little as 6 ppm of methylmercury in brain cells causes irreversible brain damage. Nobody knows what the subclinical effects of lower levels may do to the nervous system.

In conclusion, it is true that the increased addition of carbon, nitrogen, and phosphorus compounds to our waterways has increased microbial activity. When these microorganisms are confronted with mercury they have the ability to detoxify their own environment at the expense of ours. The future for microorganisms looks good. It is time for us to take inventory on this problem before the situation passes beyond repair.

SOME COORDINATION COMPOUNDS IN BIOCHEMISTRY *

J. C. Bailar, Jr.

In 1601, the French philosopher Pierre Charron wrote in his *Traité de la Sagesse*, "Le vray science et le vray étude de l'homme c'est l'homme." A century later, the oft-quoted Alexander Pope paraphrased this only slightly when he wrote, in his *Essay on Man*, "The proper study of mankind is man." Both Charron and Pope were advocating the study of man from the sociological point of view, but modern scientists have broadened the statement to include the biological aspects of man as well. In particular, chemists of most varied training have involved themselves in the study of biological phenomena. The very beginnings of chemistry were efforts to find the Philosopher's Stone and to discover the Elixir of Life, which would maintain man's youthful vigor forever.

The earliest organic chemists applied themselves to the study of drugs and nostrums and, while their treatments doubtless killed many people, they did discover some useful remedies. In much more recent times, physical chemists have applied themselves with great energy to the problems of biochemistry with their studies of light scattering by proteins, crystallography of proteins and enzymes, electron spin resonance measurements involving spin labeling, and nuclear magnetic resonance studies on the location of protons in the active centers of enzymes.

Metals in biological phenomena

Biochemists have long known that living bodies contain small amounts of metallic elements and have sought to learn the structures and functions of the compounds that contain these metals. In very recent years, this has become an exciting part of inorganic chemistry as well. The growth of this field of science was first formally recognized by the Australian National University in the appointment of the late Frank P. Dwyer as Professor of Bioinorganic Chemistry. While that title is probably still unique, more and more inorganic chemists have been devoting their efforts to the study of the role of metals in biological phenomena and the structures of the complex metal-containing compounds. Even the public press frequently carries storeis about the influence of metal salts on public health. Unfortunately, these stories emphasize the harm metals can do rather than the fact that many of them are beneficial and even necessary for life.

A few years ago we heard a great deal about the danger of strontium-90 from the fallout of nuclear explosions. Today mercury is being found with increasing frequency in our rivers and lakes, in the atmosphere, and even in the ocean. A small portion of the mercury in the rivers and lakes doubtless comes from natural sources, but most of it comes from paper mills, where phenolmercuric acetate is used as a fungicide to prevent cellulose rot, or from spillage and leakage from plants that manufacture chlorine. In the latter case, the metallic mercury sinks to the bottom of the lake or river, but bacteria convert it, through the agency of methyl cobalamin, to soluble, metallo-organic compounds, which are highly toxic. These compounds in the water are concentrated by fish, which can stand a much higher percentage of mercury than humans can. It also concentrates in fish because the half-life of mercury compounds in fish is from 500 to 1,000 days (but in man, only 70 to 74 days). Mercury in the atmosphere comes from the processing of mercury in mines and mills and from the hydrogen that escapes from chlorine plants. Although the vapor pressure of mercury is quite low at ordinary temperatures, it is appreciable, and the hydrogen that is liberated from the chlorine plant is often saturated with mercury vapor.

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* Published in American Scientist, 59, 586 (1971).

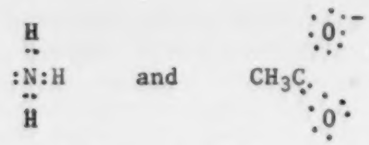
We get mercury into our bodies in other ways too. Seed grain in the United States, and in some other countries, is commonly treated with methylmercuric acetate or other mercury salts, which act as fungicides and protect the seed from rotting in the ground. The mercury is absorbed by the seed and then concentrated in the grain of the crop. When chickens eat this grain, the mercury concentrates in the eggs and, of course, when the eggs are used for human consumption, the mercury is carried into the body.

The strontium and mercury which I have mentioned are not necessarily present as coordination compounds, but they illustrate an important aspect of the role of metal compounds in biochemistry.

In this lecture, we are more concerned with the problems and importance of chelated metals and chelating agents in life processes, both plant and animal. It will be worthwhile, first of all, to define a few chemical terms for those who are not chemists. Imagine an atom or positively-charged ion, A, and a non-metallic atom or ion, B. The outer electron shell of A is not filled, so it can accept additional pairs of electrons, and that of atom B has a pair of electrons which it can share with A. If the two are brought together, electron sharing will take place, and a chemical bond will be formed between A and B:

$$A \; + \; :B \rightarrow A:B$$

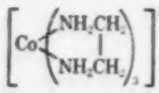
This is a coordinate bond, and the "donor" atom, B, is said to be coordinated to the "acceptor," A. In the cases which we shall consider, A can accept several pairs of electrons, so several B atoms can be coordinated to it. The number so held is the coordination number of A. Coordination numbers from one to twelve are known, but the common ones are four and six. Such entities as $[A(:B)_4]^{n\pm}$ and $[A(:B)_6]^{n\pm}$ are thus formed. Now, B may be a simple, monatomic ion, like Cl^-, but more generally it is part of a larger molecule or ion, as are the nitrogen and oxygen atoms in ammonia and the acetate ion,

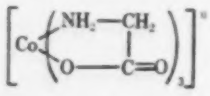


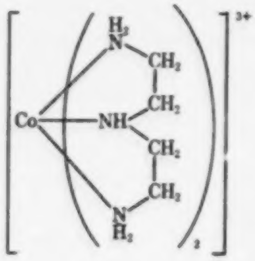
$\mathrm{H{:}\overset{\displaystyle H}{\underset{\displaystyle H}{\ddot{N}}}}$ and $\mathrm{CH_3C(O)O^-}$

A single molecule may contain two or more potential donor atoms, and if these are properly situated, they will tend to combine with the same metallic ion, forming a heterocyclic ring. In 1934, Sir Gilbert T. Morgan coined the word "chelate" to describe such rings, deriving this term from the Greek χηλή or chela, meaning *a crab's claw*, because the two donor atoms, reaching toward the acceptor, reminded him of the claws of a crab. The process of forming a chelate ring is called "chelation" and the donor molecule is often referred to as the "chelating agent."

In general, at least when the chelate ring consists of five or six atoms, chelate complexes are very much more stable than similar, nonchelated ones. If the chelating agent furnishes two atoms to the metal ion, it is said to be "bidentate; if it furnishes three, it is "terdentate, and two fused rings are formed with still further increase in the stability of the donor-acceptor bonds. Similarly, there are tetradentate and pentadentate chelating agents. In many complexes, the metal ion is part of two or three chelate rings:







Important metals

Chelating agents are widely prevalent in nature and are more powerful than is generally believed. Certain strains of soybeans growing in alkaline soil generate and secrete into the soil chelating agents that solubilize the iron needed by the plant *(1)*. Similarly, mosses and lichens growing on solid rock extract the metals necessary for their growth through chelating agents which they generate *(2)*. Microbiologists have often observed that bacteria growing in stainless steel culture tanks etch the steel in order to get the iron which they need for growth *(3)*. The conditions under which bacteria can grow are tremendously diverse and surprising. The organism, gallionella, grows best at the strongly acid pH of 2.

In this connection, we can classify the metals into five groups *(4)*:

1. Those metals which are essential to life but are not held firmly in coordination compounds, e.g. sodium, potassium, magnesium, and calcium. As an aside, I might mention that some dental caries are thought to be caused by the solubilization of the calcium in the teeth by sugar acids formed in the mouth by the oxidation of sugars *(5)*. The sugar acids, like other α-hydroxy acids, are powerful chelating agents.

2. Those metals which are essential to life and present in the body in the form of complexes. This group includes all of the metals in the first transition series from vanadium to zinc (and maybe titanium) and also molybdenum from the second transition series. Many soils are deficient in cobalt, copper, zinc, and molybdenum, and the plants that grow in them are likewise deficient. This may not be important in the growth of the plant, but it may become important if the plants are used for human or animal food. For example, sheep raisers in Australia have known for many years that the sheep became ill if they grazed in certain areas. This illness, called "sheep-sick," was finally traced to a deficiency of cobalt in the soil, and hence in the grass which grew there. The difficulty was quickly rectified by sprinkling the soil with solutions of cobalt salts, but this had to be done periodically and was inefficient in the use of cobalt. The problem is now avoided by forcing each sheep to swallow a pellet of cobalt metaland a small screw. These objects, being heavy, remain in the rumen indefinitely and give the animal all the cobalt it needs. The screw rubs against the pellet of cobalt and thus prevents it from becoming covered with an insoluble coat. When the sheep dies or is slaughtered, the cobalt pellet is recovered and given to another sheep--it may even become a family heirloom.

3. Those metals always present in plant and animal tissues and believed to have a biological function. This group includes rubidium, boron, aluminum, strontium, and barium. Boron is essential to plant growth, but perhaps not to mammals.

4. Those metals without known function and believed to be contaminants--silver and lead.

5. Those usually not detected in infants, but accumulated from the environment: e.g. cadmium, tin, lead, and, in some areas, gold, bismuth, and, rarely, germanium. Interestingly enough, chromium is found in the bodies of infants in two or three times the concentration that it is found in the bodies of adults. No explanation for this is known. The amounts of cadmium, tin, lead, and other metals which we get from our environment tend to increase in amount as we grow older and may ultimately bring on chronic disease, either through their own action or by displacing essential metals in the body. Thus, cadmium or mercury might replace zinc.

Cadmium is never found in the bodies of infants or of rural natives in Africa, and we probably acquire it from the use of galvanized iron dishes. Galvanized iron, of course, is iron coated with zinc, but commercial zinc always contains a small amount of cadmium which we apparently absorb and do not eliminate. Tin probably comes largely from the use of tin cans and other tin-plated vessels. Even in ancient times, lead was widely used in water systems, and people accumulated lead from these sources. It has been suggested that the decline of ancient Rome was brought about by lead poisoning from the use of water that came through lead aqueducts. Since it was only the better educated and wealthier people who obtained water in this way, the upper classes were more seriously affected than the less affluent. In recent times, lead for water pipes has been largely replaced by iron and steel. With our modern technology, pipes could perhaps best be made of plastic, but many building codes forbid this.

"Painter's colic," which was common even a generation ago, was a form of lead poisoning from which painters often suffered. It usually resulted from careless habits--the painter ate his lunch without carefully cleaning the paint from his hands or perhaps smoked a cigarette to which bits of paint had been transferred from his fingers. Similarly, "printer's consumption" was a form of lead poisoning from which typesetters and printers often suffered as a result of working in poorly ventilated shops.

Human patients who suffer from hypertension, when treated with certain chelating agents often show a relief of symptoms and, at the same time, their urine shows an increased content of zinc, manganese, vanadium, lead, nickel, tin, and especially cadmium, which may increase forty-fold. There is no increase in the percentage of molybdenum, chromium, silver or titanium *(6)*. Whether the relief of symptoms is related to the elimination of cadmium has not been established, but it is known that cadmium is an inhibitor of several mammalian enzymes *(7)*.

Trace metals concentrate in certain parts of the body either because that is where they play an essential role or because they are transported to that spot and can't be eliminated. Thus, manganese seems to accumulate in the pancreas, copper and molybdenum in the liver, and zinc in the prostate glad. For some strange reason, the concentration of these trace metals varies over a wide range from individual to individual. For example, the concentration of zinc in human brains has been found to vary from 480 to 1,500 parts per million, and the percentage of cobalt in lungs from 4 to 104 parts per million *(8)*.

Metal complex functions

The chelated metallic ions that are essential to life serve a wide variety of functions and each chelate is designed specifically for its function. These functions may be classified as follows:

1. Transfer of materials. This includes such diverse functions as the transport of oxygen by hemoglobin in the blood, the removal of excess iron from the system,and the introduction of iron into plants through its solubilization by chelating agents. These may be synthesized by the plant

itself, as already mentioned, or may be synthetic materials. Thus the iron(II) complex of ethylenediaminetetraacetic acid (EDTA) is used in large amounts in the citrus groves of Florida in the treatment of chlorosis, a plant disease that comes from a deficiency of iron. Simple iron(III) ions, in an alkaline soil, precipitate as the hydroxide and are not available to the plant. The EDTA complex, however, is soluble and readily enters the roots of the tree, after which the iron is converted into a form in which the tree can utilize it. As much as a half pound of the complex is often used each year for each tree.

The chelate moiety in hemoglobin is heme, the structure of which is shown in Figure 1.

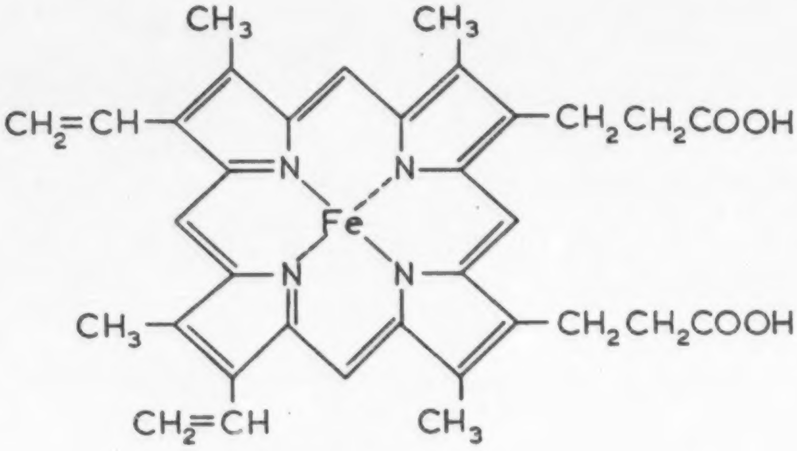


Fig. 1. The structure of heme

The entire structure is planar, and the four nitrogen atoms form a square about the iron ion, which thus becomes a member of four fused chelate rings and is held extremely tightly. Structures of this type are called porphyrins--they are common in both plant and animal bodies. Different porphyrins contain different metals, and each porphyrin has different substituent groups on its periphery. The coordination number of iron is six, so, in the heme structure, it can still attach itself to two other groups. One of these groups is globin, which is a proteinaceous material and which gives the hemoglobin the right physical and chemical properties for our use. The sixth spot in the coordination sphere is left open for combination with an oxygen molecule in the lungs. The oxygenated hemoglobin is transported by the blood from the lungs to other parts of the body.

2. The transfer of energy. Energy may be transported through the animal system in a variety of ways. For example, it may be through oxidation and reduction processes. Hemoglobin absorbs oxygen from the atmosphere and releases it to the body without any change in the oxidation state of the iron in the porphyrin, but in this process other porphyrins (the cytochromes) undergo reversible changes in the oxidation state of the iron which they contain. All six of the coordination positions in the coordination sphere of the iron in the cytochromes are filled.

Cytochromes cannot combine with donor groups, but, because of their resonating structures, they can transmit electrons.

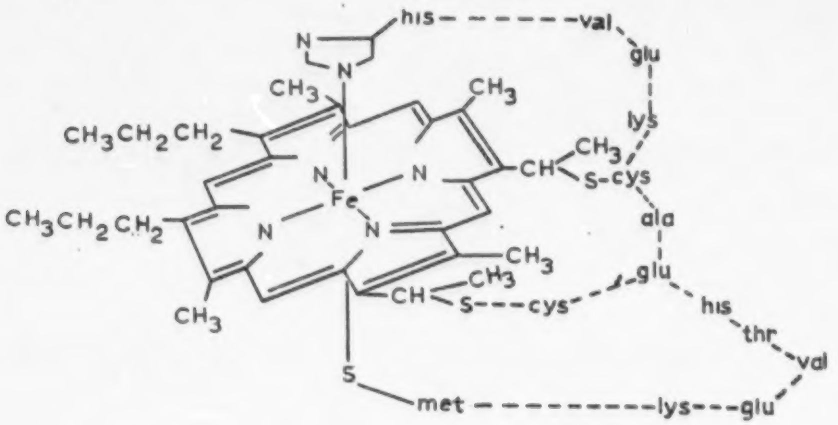

his
val
glu
lys
N
CH3
CH3CH2CH2
CH3CH2CH2
Fe
CH
S-cys
ala
glu
CH3
S---cys
his
thr
val
S
met
lys---glu

Fig. 2. The structure of cytochrome-c

Oxygenated hemoglobin oxidizes the ferrous iron in cytochrome-a and -a_3 to the ferric state. This in turn oxidizes cytochrome-c and simultaneously supplies energy for the combination of inorganic phosphate to adenosine diphosphate to form adenosine tri-phosphate. (The later reversal of this reaction liberates energy for muscular activity.)

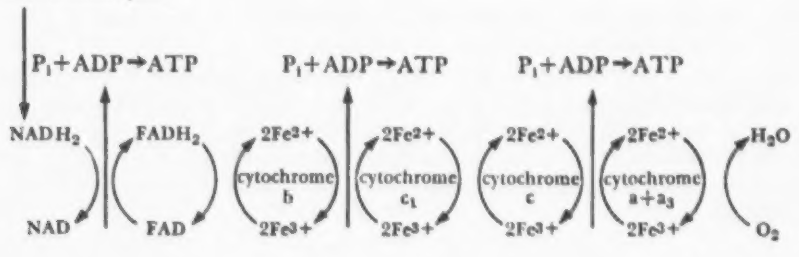

Citric acid cycle
P₁+ADP→ATP
P₁+ADP→ATP
P₁+ADP→ATP
NADH₂
NAD
FADH₂
FAD
2Fe³+
2Fe²+
cytochrome b
2Fe²+
2Fe³+
cytochrome c₁
2Fe²+
2Fe³+
cytochrome c
2Fe²+
2Fe³+
cytochrome a+a₃
H₂O
O₂

Fig. 3. Transport of energy through the cytochromes

The ferric iron in cytochrome-c oxidizes the ferrous iron in cytochrome-c_1, which in turn oxidizes the ferrous iron in cytochrome-b to the ferric state. Here, again, some energy is used to convert adenosine diphosphate to the triphosphate. The ferric iron in cytochrome-b oxidizes the iron in flavin adenine dinucleodide hydride to flavin adenine dinucleodide itself. This in turn oxidizes nicotinamide adenine dinucleodide hydride to nicotinamide adenine nucleodide, again releasing some energy for the formation of adenison triphosphate. The supply of nicotinamide adenine dinucleodide hydride is restored from the citric acid cycle in the body. The oxidation-reduction potential of the iron in each of the cytochromes differs from the next one in the series by about 0.2 of a volt, the difference in oxidation potential from the first member of the chain to the last being a little over 1 volt. Whether Nature did not know how to carry out this oxidation in one step or whether she felt that our bodies could not stand such a sharp change in voltage, we do not know. In any event, she chose to carry out the process through this interesting multi-step process.

Still another porphyrin which is very similar to heme is peroxidase, a function of which is to decompose peroxide. The protein molecule in peroxidase, which replaces the globin in hemoglobin, is attached to the porphyrin both through the iron and through the organic ring system. The porphyrin portion of the molecule is almost completely enveloped by the protein, as shown in Figure 4.

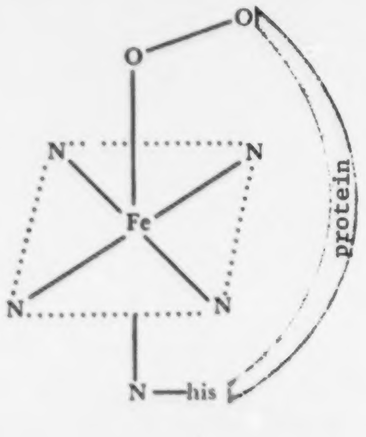


Figure 4. The structure of peroxidase

The energy which is transferred through the system may be carried by photochemical reactions, e.g., through the agency of chlorophyll in the leaves of green plants. Chlorophyll is also a porphyrin, but it contains magnesium instead of iron and the substituent groups on the periphery of the big, flat molecule are quite different. In this case, as with the other porphyrins of biological interest, a protein is attached to the metal. The function of chlorophyll is to absorb sunlight and bring about the combination of carbon dioxide and water to form sugars, which eventually become cellulose in the body of the plant. Simultaneously, oxygen is released from the leaves of the plant; but still another porphyrin is necessary to catalyze this process. This is the manganese(III) compound, shown in Figure 6, in which the protein part of the molecule is indicated by the letter X.

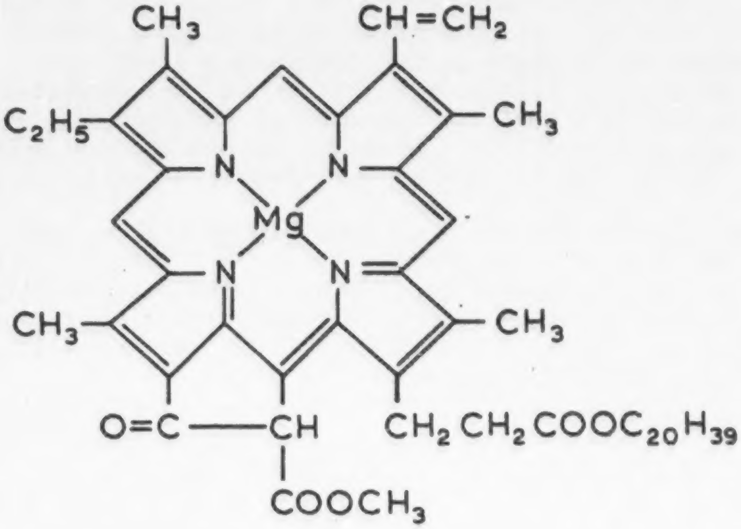

CH3
CH=CH2
C2H5
CH3
N
N
Mg
N
N
CH3
CH3
O=C
CH
CH2 CH2 COOC20H39
COOCH3

Fig. 5. The structure of Chlorophyll-a

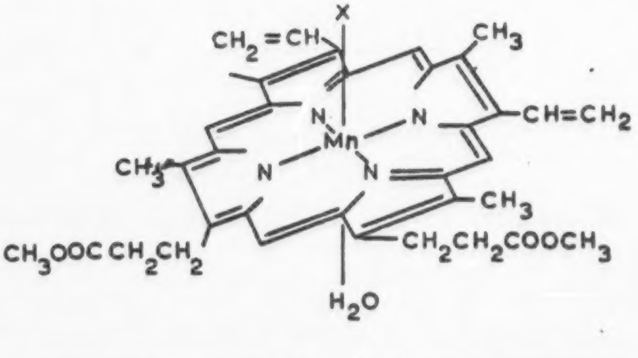

X
CH2=CH
CH3
N
N
Mn
N
N
CH=CH2
CH3
CH3
CH3OOC CH2CH2
CH2CH2COOCH3
H2O

Fig. 6. The structure of manganese(III) protoporphyrin IX dimethyl ether

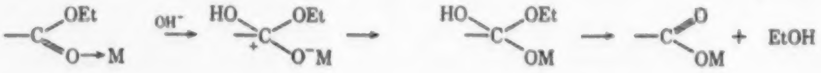
3. Some chelating materials in the body are designed to store iron until it is needed for bodily functions. These will be discussed a little later.

The metal-containing compounds involved in biological processes are of many kinds--far too many to discuss in a short article. I have arbitrarily chosen to describe three groups of compounds, not because they are more important than the others, but simply because they have been of more interest to me. These are the porphyrins, the metal-containing enzymes, and the metallo-proteins. This leaves out such important complexes as DNA and RNA and many others.

Enzymes

A vast number of metal-containing enzymes play a wide variety of catalytic roles in biochemical systems. Many of them depend upon the presence of manganese, several oxidases contain copper, there a number of zinc complexes, and at least one which contains cobalt. The enzymes offer a bewildering array of structures, but there is among them a basic, underlying pattern. In many cases, the metal can be removed from the enzyme with complete loss of its catalytic function, but the functionality is restored by putting the same metal or another back in. Commonly, replacement by a different metal gives an enzyme of much lower activity. However, replacement of the zinc in carboxypeptidase by cobalt gives a much more efficient enzyme than the naturally-occurring one. Just why Nature didn't use cobalt in the first place is a mystery. Maybe cobalt was not available when this enzyme was developed. Maybe Nature simply made a mistake.

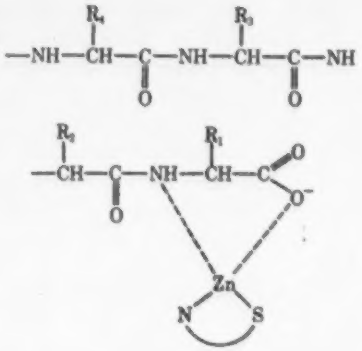
In some cases, the metal ion alone can catalyze the same reaction as the metal-containing enzyme, so the metal is often considered to be the site of the catalysis. However, the naked metal ion is nearly always far less effective than the enzyme. The main function of the metal ion is to draw electrons from the substrate toward itself and thus weaken bonds in the substrate *(9)*, as illustrated by the equations



Of course, stereochemical and other factors play important roles in the behavior of the enzyme, also. Cornforth *(10)* has shown the importance of steric factors by a most ingenious method. He prepared acetic acid in which the methyl group contained one atom of hydrogen, one of deuterium, and one of tritium. Thus, it is asymmetric. It can be converted by enzymatic action into acetoacetic acid and thus to acetylcoenzyme A. This is used in the synthesis of fatty acids. However, the two enantiomorphic forms of the enzyme give quite different results.

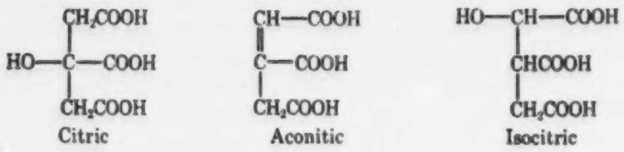
In general, enzymes are highly specific. Thus, the zinc enzyme chymotrypsin hydrolyzes tyroslyglycine, but carboxy peptidase, which is also a zinc complex, hydrolyzes glycyltyrosine *(11)*. These two enzymes are different enough to cause them to behave in very different ways. In a splendid article on the mechanism of enzyme action, Sigel and McCormick have made the following observations *(12)*: (1) The metal ion may induce, by coordination, a specific "lock" geometry of the apoprotein metal binding site, so that only certain substrates can be attacked. (2) The metal ion may activate a bond (or bonds) of the substrate or protein through coordination. (3) The metal ion may induce, by coordination, a specific "key" geometry of the substrate, so that it will fit the "lock" of the apoproteins specifically.

Carboxypeptidase-A has been studied more than any other enzyme and its structure is fully known. Its function is to cleave the peptide bond adjacent to the terminal carboxyl group of the protein molecule as illustrated by the formula



The zinc atom in the enzyme is able to combine with the terminal carboxy group and the adjacent nitrogen atom, but not with the amide carbonyl groups. Electrons are drawn from the amide group toward the zinc, thus weakening the C-N bond so that it is readily hydrolyzed. This, of course, generates a new terminal group, and the process can be repeated. Carboxypepsidase-A contains one zinc ion per molecule of enzyme. This zinc ion can be removed by dialysis against a strong coordinating agent like ortho-phenylenediamine with complete loss of catalytic activity. The activity can then be restored by addition of zinc ion or by other divalent ions, such as Mn^{2+} , Co^{2+}, Fe^{2+}, or Ni^{2+}.

Another enzyme, aconitase, has the ability to interconvert citrate, isocitrate, and aconitate, the structures of which are shown in Fig. 7.



Citric Aconitic Isocitric

Fig. 7. Citric, aconitic and isocitric acids

These conversions are brought about through the agency of the iron(II) which is contained in the enzyme. The generally-accepted mechanism is shown in Figure 8 *(13)*.

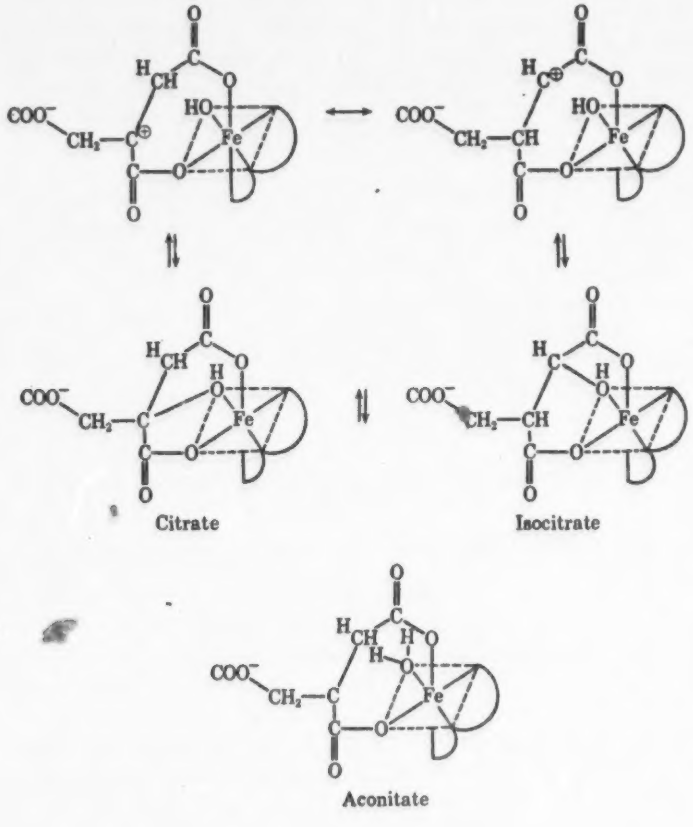

Citrate
Isocitrate
Aconitate

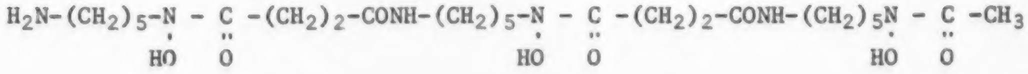
Fig. 8. Mechanism of the aconitase reaction

Metallo-proteins

The third and last group of compounds which I shall mention consists of the metallo-proteins. These substances serve some of the same functions as the porphyrin complexes, but they do not contain prosthetic groups. They are much less well understood than the other bio-coordination compounds that have been discussed here. Hemerythrin resembles hemoglobin in that it carries molecular oxygen through the living system --not in the human body, but in the bodies of sipunculid worms. The molecular weight of hemerythrin is about 107,000. The molecule consists of eight polypeptide sub-units, each of which contains two atoms of ferrous iron. Each peptide chain can hold one oxygen molecule. As is the case with hemoglobin, the iron in hemerythrin remains in the ferrous condition when it is oxygenated. The oxygenated ferrous form, however, can be oxidized to the ferric state by ferricyanide and reduced back to the ferrous condition by dithionite.

Since we require iron for several biological functions, Nature has provided a mechanism for storing it in the body. This is effected through the metallo-protein ferritin, which forms very stable chelate complexes with iron(III). The usual content of iron in ferritin is from 17 to 23 percent, but on occasion the level far exceeds this. A single molecule of ferritin can hold as many as 4300 atoms of iron.

The iron which one ingests is carried in the blood stream to various parts of the body by another metallo-protein, called transferrin, from which it is transferred to the ferritin. Transferrin is a strong complexing agent for iron(III), but, since it must release its iron to the ferritin, it is not as strong a chelator as the latter. Ferritin liberates iron to the body only by decomposition. If, through ingestion of excessive amounts of iron, one gets too much iron in the system, the body generates a chelating agent known as deferoxamine, which is an amazingly powerful and specific coordinating agent for iron *(14)*. Its structure is shown in Figure 9. It is able to extract iron from nearly all of the tissues of the body, but not from transferrin or ferritin.



$$H_2N-(CH_2)_5-\underset{HO}{\underset{\cdot}{N}} - \underset{O}{\underset{\cdot\cdot}{C}} -(CH_2)_2-CONH-(CH_2)_5-\underset{HO}{\underset{\cdot}{N}} - \underset{O}{\underset{\cdot\cdot}{C}} -(CH_2)_2-CONH-(CH_2)_5\underset{HO}{\underset{\cdot}{N}} - \underset{O}{\underset{\cdot\cdot}{C}} -CH_3$$

Fig. 9. The structure of deferoxamine

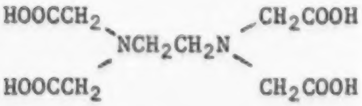
This is illustrated by the figures in Table 1, which also includes figures for several strong synthetic chelating agents. Their structures are listed, for comparison, in Table 2.

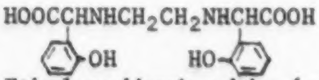
Table 1 shows that the stability constant of the iron(III)-deferoxamine complex is higher than that of any of the synthetic iron(III)-chelating agents which are listed except ethylenediamine-di-(o-hydroxyphenylacetic acid) (EDDHA). It is, however, much more highly specific for iron(III) than is EDDHA. The only synthetic material which rivals it in the tenacity with which it holds iron(III) and in specificity is the synthetic material N,N-bis-(hydroxyethyl)-glycine (Fe-3-specific). Not only is deferoxamine highly specific for iron(III), but its water solubility allows it to get into intra- and extra-vascular spaces, but excludes it from intercellular space. Its lipid solubility allows it to enter cells and enhances non-renal secretion, such as into the bile *(14)*.

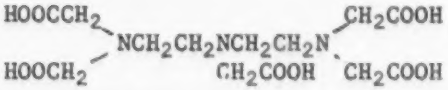
Table 1. Logs of some stability constants (from *Reference 14)*

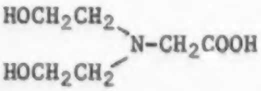
Chelating agent	Fe^{3+}	Fe^{2+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Mn^{2+}	Cu^{2+}
EDTA	25.1	14.3	10.6	8.7	16.5	14.0	18.8
DTPA	28.6	16.5	10.1	9.0	18.1	15.1	21.0
HEDTA	19.6	12.2	8.0	5.2	14.5	10.7	17.4
Fe-3-Specific	30.1	4.2	---	1.1	5.4	3.1	8.1
EDDHA	32.0	---	7.2	8.0	9.3	---	16.2
Deferoxamine	30.7	10.	1.7	4.	11.	---	14.
Transferrin	36.	---	---	---	---	---	---

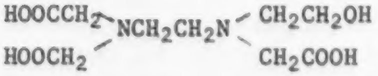
Table 2. Structures of some chelating agents


Ethylenediaminetetraacetic Acid
EDTA


Ethylenediamine-bis-(o-hydroxyphenylacetic acid)
EDDHA


Diethylenetriaminepentaacetic acid
DTPA


bis-(hydroxyethyl)-glycine
"Fe-3-Specific"


Hydroxyethylethylenediaminetriacetic acid
HEDTA

Ceruloplasmin *(15)* is a copper protein complex of molecular weight of about 150,000. Each molecule contains eight atoms of copper, four of which are bound more tightly than the other four. Both copper(I) and copper(II) are present, and there is some evidence that they are there in equal amounts. The biological function of ceruloplasmin is not well understood, but it is probably to store copper in the body. This supposition is supported by studies of Wilson's disease, which is due to a hereditary deficiency in ceruloplasmin. Patients suffering from Wilson's disease have an accumulation of unbound copper in their bodies.

Vitamin B-12, sometimes known as coenzyme B-12, is an essential vitamin structurally related to the homoproteins. The structure is shown in Figure 10.

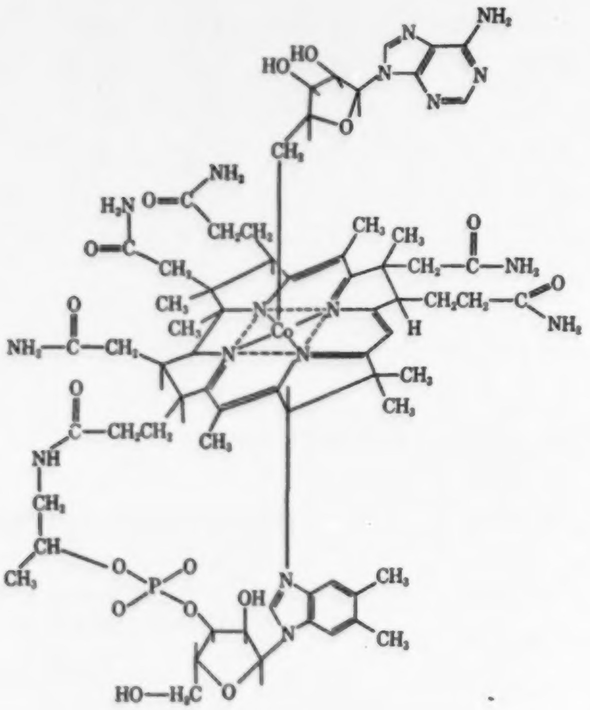
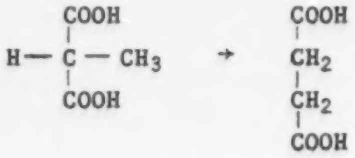


Fig. 10. The structure of vitamin B-12

Vitamin B-12 contains four pyrrole rings, as does heme, but these rings are partially reduced, whereas in heme they are fully conjugated. Also, in heme, the groups binding the pyrrole rings together are all alike, but in Vitamin B-12, one bridging -CH- group is missing, so there is a five-membered ring in place of a six-membered ring. There is also, remarkably enough, a direct cobalt-carbon bond. The cobalt is in the +3 state, but is easily reduced to the +2 state. In vitamin B-12_s, it is in the +1 state. Vitamin B-12 brings about molecular rearrangements, moving an organic group from one carbon atom in the substrate to another. Thus, it is able to bring about the conversion of methylmalonic acid to succinic acid *(16)*.



$$\mathrm{H{-}C(COOH)_2{-}CH_3} \rightarrow \mathrm{HOOC{-}CH_2{-}CH_2{-}COOH}$$

Methylcobalamin, which contains a methyl group in place of the 5′-deoxyadenosyl group shown in Figure 10, is a strong methylating agent, and it is this substance that brings about the methylation of mercury that was mentioned in the early part of this article.

Although this is a brief and woefully incomplete report on a few coordination compounds which are found in biological media, perhaps it will stimulate the interest of the reader in the subject so that he will wish to study it further.

I am grateful to Dr. Gunther Eichhorn, Dr. Nicholas Matwyioff, and Dr. John Wood for many suggestions.

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TRACE METALS AND ANIMAL GROWTH AND LONGEVITY

R. M. Forbes

It is my aim to treat the subject of trace metals and animal growth and longevity from the point of view that development of knowledge in this area took place only as the broader aspects of nutrition, biochemistry, and analytical chemistry advanced. I hope to illustrate the interdependence of nutritional advances on development of its several supporting sciences and at the same time present a generalized view of the importance of trace mineral elements in animal metabolism.

In the early eras of nutrition research the major interest was in energy and protein for the very good reason that, in a quantitative sense, the nutritional requirements of animal life are dominated by a need for energy and for amino acids. Indeed, once our energy requirements are met by dietary carbohydrate and fat, and our amino acid requirements by dietary protein, we have accounted for over 95% of our total food intake. Most of the remaining few percent of a good diet or animal feed consists of the major inorganic nutrients: Ca, P, Na, K, Cl, Mg, and Fe.

The completion of the diet requires about 0.15% of trace organic nutrients which we call vitamins, and something less than 0.1% of the trace inorganic nutrients--which are the subject of today's seminar. One-tenth of one percent may not appear to be a very large number. Perhaps if we call it 1000 ppm it will look larger. Yet, when we consider the probable requirement for individual trace inorganic substances--for example, 10 ppm for Zn, or less than 0.1 ppm for Se or Cr--we can understand the use of the word "trace" in this connection.

Progress in this field was impossible before the necessary tools were developed. Good analytical procedures are required. Biochemical techniques must be advanced to the point that enzyme and membrane transport mechanisms can be studied, since these are the mode of action of most of the trace elements. Nutritional knowledge must be advanced to the point that diets can be prepared, adequate in all respects but the trace metals, so that the specific effects of their individual deficiencies can be studied and the interactions between the trace nutrients can be clarified.

One of the authorities in the field, Walter Mertz at Walter Reed Army Hospital, has said (Mertz, 1970), "It is the ultimate aim of nutritional trace element research to assure the population of an optimal dietary intake of essential elements and to prevent the overexposure to others." I would modify this statement only to recognize that overexposure to the essential elements can also be a matter of concern.

The origin of the interest of animal biologists in the beneficial effects of trace metals may be said to be derived from two separate lines of observation. First, as a result of finding many of these elements in animal tissues and in specific metallo-organic compounds in animal tissues. The fact of their presence led to the obvious question: "What are they doing there?" The second approach derived from observation of failure of grazing animals to thrive on what appeared to be nutritious pasture and rangeland. A more specific, and the first recorded, type of observation was that goiter is a geographically-oriented disease, afflicting animal and human alike, and that it can be prevented by feeding moderate amounts of ocean salts. These studies date back 100 years or more, but were in themselves not particularly revealing, since the techniques for following up on them were not yet developed.

These studies did, however, provide the spark that led to early attempts to manipulate the trace element content of experimental diets for animals. These early experiments were largely significant in terms of failure since, in efforts to purify diets sufficiently to obtain low mineral levels, many of the vitamins were left out or destroyed. In those days (about fifty years ago) most of the vitamins remained to be discovered, although it was realized that a variety of natural food ingredients, such as crude extracts of liver or yeast, and of green plant tissue, did supply some sort of nutrient essential. In efforts to devise low trace mineral diets by leaving out these natural ingredients, the vitamins were also left out. As a consequence, the experimental animals could not respond to mineral supplementation, since they were vitamin deficient.

One of the first really definitive experiments that resulted in production of a trace element deficiency circumvented the problem of purified diet preparation by relying on "nature's perfect food"--milk. This is a good food for young mammals, but it was intended to be used as a sole article of diet for a relatively brief time after birth. Since prolonged feeding of milk was known to result in iron deficiency, investigators at the University of Wisconsin in the late 1920's decided it would make a good basal diet for their studies on anemia. They fed milk as the sole article of diet to young rats and found, sure enough, that they became anemic. They further found that some sources of iron salts added to the milk would prevent or cure the anemia, but that some would not. It wasn't long before they found that traces of copper, present in some of their salts, were needed along with the iron for anemia prevention (Hart *et al.*, 1928). This was the initial finding of a specific effect of copper in mammalian organisms, although it had been found in animal tissues and was known to be tightly bound in some purified proteins, for example, in hemocyanin, an O_2-carrying protein in snails and mollusks.

As our knowledge of nutrition developed it became possible to devise quite reasonably purified diets, and this technique has permitted considerable expansion of the list of essential mineral elements. Rose and group at Illinois contributed largely to the purified diet approach by the discovery of threonine.

Another useful technique in discovery of essential trace elements depended on the uneven distribution or availability of mineral elements in some soils and, hence, in the plants growing on them. Animals, particularly gracing animals, receiving their total feed from grasses and other forages growing in certain areas have been known not to perform well in spite of the presence of adequate quantities of feed (Beeson, 1958). Not long after the Wisconsin story relative to copper became known, investigators at the University of Florida were encouraged to feed copper to cattle grazing in the sandy soil of that state. Up until that time cattle-raising was not successful in Florida because of frequent anemia. Copper therapy was quite useful and is, in large measure, together with cobalt supplements, responsible for the great development of the cattle industry in that state. This early demonstration (Neal *et al.*, 1931) of a trace element deficiency occurring under natural conditions has had far-reaching applications in practical animal-husbandry in many areas of the world. Another widespread problem in ruminant nutrition was found, in the mid-1930's, to result from cobalt deficiency. As a result of continuation of studies of this sort, the list of practical trace element deficiencies in grazing animals now includes Cu, Zn, Co, Se and I. We are now able to devise diets sufficiently low in other trace elements that animal performance suffers. These add to the list of essentials: Mn, Mo, Cr, Ni and V.

Much of the early work, for obvious reasons, was directed at identification and practical control of trace element deficiencies of sufficient severity to be of economic importance and to exhibit definite symptomology. Before long it became recognized that "simple" deficiencies were the exception, and that there were many areas in which deficiencies were not severe enough to produce well-defined symptoms; also that correlations between mineral content of plants and incidence of trace element deficiency was not always high. For example, copper deficiency symptoms in sheep have been found when the animals were grazing pastures of normal copper content, and copper toxicity has been seen in sheep with the same copper intake as that of normal sheep. It required very nice detective work to discover that excess molybdenum could cause copper deficiency by inhibiting entry or release of Cu into the tissues in which it is used, and that a combined deficiency of molybdenum and a low sulfate intake could produce copper poisoning (sudden release from liver with consequent hemolysis, jaundice, and death), since a combined action of these materials is necessary to prevent copper accumulation in the tissues (Underwood, 1970).

Within the past twenty years empirical approaches have given way to more definitive studies on biological function and kinetics of the trace elements in animal bodies. These have revealed many of their functions to be catalytic in nature. Some enzymes are metallo-proteins and contain specific metals, i.e., zinc in dehydrogenases, Cu in oxidases. Other enzymes function as protein-metal complexes, requiring the metals for activation; these requirements are less specific, i.e., Mn-stimulated phosphorylases and carboxylases can also be activated by Mg in absence of Mn (Eichorn, 1960). In spite of our ability to describe such specific roles to some of the trace elements, the physiological effects of trace element deficiencies are most often observable without important changes in enzyme function, so far as we can detect them. Exceptions to this are the single unique functions of iodine and of cobalt, as structural constituents of thyroxine and of vitamin-B_{12}. A typical example of the general rule is, that zinc deficiency becomes apparent in terms of poor growth in just a few days after animals are placed on a zinc-deficient diet and before any changes in enzyme level can be detected, resulting in symptoms such as severe dermatitis and delayed development of male sexual maturity, which are not yet explainable in terms of known enzymic malfunction.

Another type of function may be to effect transport of metabolites across membranes. It has been suggested, for example, that the anti-diabetic function of chromium is a result of its aiding the insulin-dependent transport of glucose across cell membranes (Mertz, 1969), and that molybdenum inhibits transfer of copper across cell membranes.

Nutritional effects of trace metals on fetal growth and development:

In looking at some of the more specific aspects of nutritional effects of trace metals--and we can only scratch the surface of this area--one of the critical times when an adequate supply of these is important is during fetal growth and development. The nutritional aphorism that the fetus will develop at the expense of the mother has a certain truth to it; but this does not apply completely to the trace metals.

One of the earliest examples of this was recognition that a deficient supply of iodine to the mother will result in birth of young with all of the symptoms of defective thyroxine supply, since iodine is an essential constituent of this hormone. Baby pigs, sheep and horses born under conditions of insufficient iodine in their mother's diet will have low growth rate and viability. This may occur even though the mother does not exhibit signs of iodine deficiency. In humans, cretinism will result, and the child's physical and mental development will be permanently impaired. This has been a widespread practical problem in scattered areas of the entire world and the practical solution has been known and applied for many years. The use of iodized salt for both livestock and humans has been an extremely valuable practice.

Two other good examples of the importance of mineral nutrition during fetal development may be found in the work of Dr. Lucille Hurley at the University of California at Davis. She has very convincingly demonstrated the extreme vulnerability of the fetus to nutritional trace metal deficiency (Hurley, 1967). It has been demonstrated in several species of animals that a maternal manganese deficiency results in young with severe problems in maintaining balance and orientation. Dr. Hurley has shown in the rate and guinea pig that this is a result of malformation of the bones of the inner ear and of its sensory epithelium which is responsible for the sense of balance. She has further shown that, in the rat the development of this area is closely programmed in the scheme of development and that interference with this program is not repairable. In her studies she raised female rats on a milk diet fortified with Fe, Cu and I. This diet was deficiency in Mn, but contained enough to permit the females to grow reasonably well and to conceive and bear young. A high percentage of the young did not survive, however, and most of the survivors developed the ataxia of manganese deficiency. Pregnancy in the rat lasts for 21 days. Supplementation of this diet of the mother with 6 ppm Mn on day 14 only, entirely prevented ataxia in the young and increased the survival percentage greatly. Waiting until day 16 was less effective, and day 18 was too late to be useful at all. In rather similar experiments, in which female rats were raised on borderline levels of zinc, the effects on the pups were just as striking. In this work, only 44% of the females bore living young while on the zinc-deficient diet, and 98% of these rat pups had abnormalities in development of skeleton and soft tissues, even though the mothers themselves did not show obvious signs of zinc deficiency.

So far as we know, the Mn part of the story has no current application in the human situation. In the case of zinc there are well documented cases of zinc deficiency in adolescents in Egypt and Iron (Prased, 1967), and although no correlation of this with birth defects in humans has been obtained, it would appear to be within the realm of possibility.

A final type of function of trace metals about which we need to know much more is inferred from the consistent presence of materials such as Cr, Mn, Ni, Fe, Cd in DNA and RNA (Wacker and Vallee, 1959). These metals may serve as ligands to determine tertiary structure and thus have a profound influence in biological functions such as protein synthesis and transmission of genetic information.

Toxic effects of trace elements

Another side of the essential trace element story relates to possible toxic effects of these nutrients and the relationship of toxic levels to optimal levels. Those elements which are known to be nutritionally useful are, for the most part, less toxic than a large number of the adventitious elements, such as: Pb, Hg, As and Cd. The ratio between optimal and toxic levels of Cu, for example, approximates 400-fold; Zn, 300-fold; Co, 1000-fold; Mn, 200-600-fold; and Se, 20-fold. These sound like large safety factors; but we need to remember that the absolute amounts indicated are measured in most cases in 10's or 100's of parts per million. The likelihood of natural occurrence of toxic levels of these named minerals is not great. There is an exception, of course, which I have already mentioned: that of copper toxicity in sheep fed low-molybdenum diets.

Another exception worthy of brief note here is selenium, which is present in some soils and concentrates in plants at levels extremely toxic to grazing animals (Muth *et al.*, 1967). This toxicity can become evident at Se concentrations as low as 5 ppm. Many seleniferous plants may contain several hundred ppm of Se. Another exception is F, which, while not nutritionally essential, is beneficial in preventing dental caries when present in either drinking water or food at a level of about 1 ppm (McClure, 1970). This level of F is perfectly safe; but there are many water supplies, in this country and elsewhere, containing 2-10 ppm F. This level will lead to discolored, brittle teeth that chip away and erode, and to abnormal calcification (over-calcification) of bones and joints. A real problem of pollution with F exists downwind from factories which, in the process of extracting aluminum from the ore, release large amounts of F to the air. This fluoride settles on pastures and concentrates at levels extremely toxic to grazing animals. Toxic levels of F have also been produced in pastures by irrigating them with highly fluoridated water.

Effects on growth and longevity

Another type of study of the effects of trace elements on animal performance is demonstrated by the studies of Schroeder at Dartmouth Medical School, who has done life-span studies with rats and mice under carefully-controlled conditions (Schroeder *et al.*, 1970). This work was undertaken largely as a result of data showing in the human population (17 elements in 11 tissues of 188 persons) that lead, titanium, cadmium and tin concentrations increase with age in kidney and liver, and that chromium concentration decreases with age in these same tissues (Tipton, 1960). In the case of chromium, the adult organs contain about 1/50 the concentration as do those of the month-old child. On the basis of this sort of evidence, Schroeder set out to try to produce, in the convenient rodent tissue, levels of a number of trace minerals similar to those found in adult humans and at the same time to see what effect these elements might have on longevity and general health. These studies have been quite extensive, and their detailed interpretation is too complex for us this afternoon. Basically, Schroeder used a well-defined diet containing low levels of the elements of interest, fed to animals in an ultra-clean environment. The drinking water was demineralized and then supplemented with 2-5 ppm of the metals of interest. The studies were carried out over the life-span of the animals.

The following metals were without effect on growth, longevity, or a number of biochemical parameters: Nickel, tellurium, and tin.

Of the 14 metals tested under these conditions, only chromium appeared to be beneficial in terms of longevity. Chromium had the added benefit of lowering serum cholesterol and of lowering serum glucose, offsetting a tendency toward diabetes in the older animals and humans. It has been shown, since this initial demonstration, that chromium is indeed an essential mineral and may even be of practical benefit in human nutrition.

Most of the other elements, *i.e.*, Ti, Pb, Cd, Se, Sn, Ge, As, NiO and Sb, reduced the average life-span of the rats or mice. Exceptions to this were vanadium and zirconium, which had no effect on longevity but did lower serum cholesterol. Lead and selenium were particularly toxic in terms of longevity; but this property of lead was minimized in the presence of chromium, thus indicating a lead-chromium interaction.

A significant feature of this work of Schroeder's is, that the longevity effects were attained in animals whose tissue mineral levels approximated those found in the general population of humans.

Another significant feature of this work, which really was no great surprise but is worthy of comment, is the toxicity of selenium (Muth, *et al.*, 1967). It is the only one of the recognized essential elements toxic at the low concentrations used in Schoreder's studies. The original nutritional interest in selenium arose as a result of its presence in toxic concentrations in soils and, hence, in forages in certain areas in South Dakota. Actually, Marco Polo in the thirteenth century described what we now recognize as the effects of selenium toxicity. It is reported that his horses became ill and lame, their hooves fell off, and many died if they ate certain plants. The identification of selenium as a toxic element was made in 1934 through studies conducted at South Dakota and Wyoming Experiment Stations. As a result of these and many subsequent studies, it is now recognized, that in about a third of the area of South Dakota, and smaller areas in all of the bordering states south and west, forage plants may contain from a few to several thousand ppm of selenium. These areas cannot be used for livestock since, generally speaking, Se intakes of about 10-20 ppm will produce frank toxicity. Grains grown in these areas do not contain so much Se as do the leafy portions of the plant; but they do contain enough so that they cannot be used as feed for chickens or swine.

As another example of mineral interaction, I might mention that 5 ppm of arsenic in diets fed to rats, dogs and pigs has been shown to be quite effective in diminishing the toxicity of Se. This is not a practice that is likely to become one of practical application!

The selenium coin has a second, also prominent, face. Through a variety of studies with purified diets fed to laboratory animals, and observation of a spontaneous "white muscle disease" in grazing animals, selenium has unequivocally been classified as an essential nutrient. Although a specific metabolic role has not yet been found, degeneration of liver, muscle and pancreas does accompany selenium deficiency, that is, a diet containing about 0.02 ppm. One of the major problems in identifying the roles of selenium as an essential element is that the pancreatic degeneration produced by the deficiency causes a reduced secretion of digestive enzymes into the intestines, which in turn reduces the digestibility and absorption of lipids, including vitamin E, thus creating a double deficiency. Provision of rations with 0.1 ppm Se will prevent these abnormalities in animals as diverse as sheep and Japanese quail.

Zinc deficiency

A final example of the importance of studying nutrient interrelationships may be found in the zinc story (Prasad, 1966). The initial discovery of the essentiality of zinc in mammals was made at the University of Wisconsin in the early 1930's; this work indicated a probable requirement by the rat for zinc of about 3-4 ppm. This bit of information did not stimulate much additional investigation--in part because this was the heyday of vitamin discovery, and because zinc supply did not seem to be a practical problem, most natural animal rations having 10-15 times the anticipated requirement.

About twenty years later a report from the Alabama experiment station indicated that a severe dermatitis in swine which had become a widespread disorder several years previously could be prevented by adding zinc (about 50 ppm) to diets already containing 30 ppm. These workers also reported that high calcium diets exaggerated the dermatitis and increased the zinc requirement. This was a shock to those of us in the establishment, and it stimulated a great amount of work over the next ten years.

It turned out that the Alabama investigators were right; pigs fed as theirs were (and many pigs were then being so fed) do require 40-60 ppm zinc in their diets. But the puzzling question was, "Why has this zinc deficiency dermatitis appeared so suddenly?" It required the purified-diet approach to answer this question. Basically it turned out that when pigs were fed the corn-soybean-meal type of ration used todaytheir zinc requirement is about 40-60 ppm, and it increases if extra calcium is in the diet. On the other hand, if a purified diet--using starch and casein as its major ingredients--is used, the requirement for zinc is about 12 ppm; and this is as true for the pig as it is for the rat and the chick, though in this case extra calcium does not increase the zinc requirement. The key to this situation is that soybean meal contains phytic acid which, in the presence of calcium, readily chelates zinc so that it is not absorbed into the animal body. This has been demonstrated both in the test tube and by adding phytic acid to a casein-starch diet and measuring zinc absorption. Also, if one adds graded levels of calcium to the casein/starch/phytic acid diet, he can show a graded depression in zinc absorption. In the test tube, one can demonstrate that the mixed salt of phytic acid, calcium and zinc is much less soluble than either calcium phytate or zinc phytate.

Two changes in pig feeding were made during the 1940's and early 1950's that probably account for the incidence of zinc deficiency dermatitis that became prominent during the early 1950's. One was the change from importing bone meal as a supplementary source of calcium and phosphorus--because of disease organisms. Bone meal has relatively high amounts of zinc, and in its place manufacturers of pig feeds used other, non-biological, sources of calcium and phosphorus that contained little zinc. Probably a more important change was the introduction of soybean meal (and its zinc chelating properties) as a major protein source, replacing in the diet meat scraps, blood meal, and other animal products. This was made possible by the development of the soybean industry and by the discovery of vitamin-B_{12} in 1948, which was really a historic event. Until this time it was thought that pigs, chickens and people needed in their diet an unidentified substance that was absent from plant materials but was found in association with proteins. When this material was identified as vitamin-B_{12} it suddenly became possible to feed pigs and chickens the cleaner, less-expensive plant proteins, instead of meat scraps, etc. This provided more economical rations; but also gave rise to the zinc problem.

A final aspect of the mineral area that deserves at least a brief comment relates to a possible relationship between air pollution, as exemplified by carbon monoxide, and the distribution of trace metals among the subcellular fractions of animal tissues. This investigation (Mazaleski *et al.*, 1970) was undertaken on the basis that carbon monoxide is known as a pollutant and it is known that it inhibits respiratory enzymes which contain iron and copper. Thus, it was thought that chronic exposure of animals to some significant but "safe" level of CO might alter respiratory metabolism in cells enough to cause some shift in trace metal distribution. In this work, young rats were kept for 12 weeks in an air-controlled environment, half of them receiving, for 5 hours daily, 5 days a week, an atmosphere containing 50 ppm CO. Control and experimental rats were killed at 3-week intervals, their livers (representing an active body tissue) were removed. Nuclei and mitochondria were each separated from the cytoplasm and each portion was analyzed for Cu, Fe, Zn, Co, and Mg. Without going into details, I can say that mineral concentration in mitochondria did not appear to be changed by exposure of animals to this concentration of CO. Cobalt was generally decreased in all fractions, and Mg tended to be increased in nuclei and decreased in the cytoplasmic fraction. There were no clear-cut trends in change with length of exposure.

I feel that the above experiment is more important for its contribution of an original approach to the study of the effects of CO pollution, than for any new facts or relationships uncovered. This technique might well be employed in other situations of environmental stress and might also investigate distribution of other metals than the essential ones.

To summarize all of this very briefly, I have attempted to show you the breadth of our interest and the importance not only of essential trace metals in animal well-being, but some of the aspects of our concern for potentially toxic minerals, be they essential or as yet having no described function. I have given examples illustrating the interdependence of these minerals, and of the need for mutual development in the several scientific disciplines necessary for the best progress in this field of investigation. Food is an important aspect of our environment and we need to avoid its contamination while at the same time regulating its composition to optimize its usefulness.

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TRACE METALS--CADMIUM, LEAD AND COPPER IN THE BLOOD AND SERUM OF CADMIUM-DOSED RATS

Reginald Griffin

Trace metals in the environment are very important because of their direct and/or indirect effects on man. This paper, therefore, will deal with the distribution of Cadmium (Cd), Lead (Pb), and Copper (Cu) in the red blood cells and small molecular weight serum fractions of animals which were given repeated subacute doses of cadmium. The small molecular weight serum components were studied because it was felt that they would prove to be important in the initial transport of trace metals entering the blood compartment; it was further felt that they might be instrumental in the early detection of adverse effects of a heavy metal insult on a mammalian system.

Figure 1 illustrates the experimental design used in obtaining the presented data.

Five Sprague-Dawley male rats of comparable weights and ages were given repeated subacute, subcutaneous doses of cadmium (0.6 mgCd/Kgm of body weight). These animals were frequently bled over a 4-6 week period via a lateral, ventral tail vein cut. The 0.5 milliliter (ml) blood samples, from which approximately 0.25 ml of serum was derived, were not detrimental to the test animals.

Two hundred microliters (μl) of the serum sample was placed on a G-25 fine Sephadex column (M.W. exclusion 5,000) and fractionated. The collected fractions were analyzed for labile, nonlabile and total Cd, Pb and Cu content by anodic stripping voltammetry (ASV). The red blood cells were frozen for analysis at a later date.

A labile metal complex is one which has a fast dissociation rate relative to the ASV cell constant (Kc), or in other words, it is reduced directly at the electrode surface. A nonlabile metal complex is one which has a very slow or seemingly nonexistent dissociation rate with respect to Kc; hence it does not reduce directly at the electrode surface. A nonlabile metal complex must have the binding ligand digested or sufficiently altered so that the bound metals are free for analysis (total trace metal analysis). A 1200-watt U.V. light was used to accomplish the latter goal in this study. The nonlabile trace metal content of a sample is found by subtracting the labile metal content from the total metal content.

The significance of labile and nonlabile metal complexes in a biological system may be considered in the following way. A labile metal complex, because it exhibits rapid exchange kinetics, might be referred to as an intermediate transport complex--Intermediate between the site of metal introduction and the site of final transfer, either a nonlabile organic ligand (e.g. albumin) or a deposition depot (e.g. bone, cells, etc.). A nonlabile metal complex has slow exchange kinetics and could be considered a safety mechanism for a biological system. Any metals bound in such a complex would conceivably be released very slowly for cellular uptake, hence, the system would be spared an acute exposure situation and could work on the elimination of said material. This would hold primarily for low level aperiodic heavy metal exposures, because the system could still be overwhelmed by large acute and continuous "low" level exposures. Thus, we see that the complexation state of a metal is every much as important as the quantity present.

The conversion factors for Cd, Pb and Cu are 0.6 nanograms per microampere, 0.85 nanograms per microampere and 0.63 nanograms per microampere respectively. These values are useful in the interpretation of the graphic data presented in this paper.

Figure 2 shows the labile distribution of cadmium in the serum of rat number 1 on day number 1. The major point of interest is the amount of Cd associated with the intermediate molecular weight serum components. Figures 3 and 4 show that Pb and Cu are two other metals which bind with labile ligands in the intermediate sizes; their variations are possibly related to the Cd injections as no Pb or Cu was ever intentionally given. When rat number 1 was sampled on day 4 the Cd associated with the intermediate size ligands was no longer present (Fig. 5); there were two elution peaks in the small molecular weight region, however. Figure 6 shows a change in the lead spectrum of rat 1 on day 4. The distribution of labile Cu (Fig. 7) showed change from day 1, yet it was not one of decreased concentration, but rather of peak positions. The Pb and Cu ligands may be the same as those binding Cd.

On day 12 (Fig. 8), the intermediate weight Cd ligands reappeared for rat 1; the lead remained depressed (Fig. 9), and the copper showed signs of having decreased (Fig. 10).

All of the analyses for rat 1 were labile, because random sample digestion and denaturation with U.V. light showed no change in fraction metal concentration. This all-labile-bound metal phenomenon was of particular interest because none of the other four test animals demonstrated it, and because rat 1 died on day 18 of the study, whereas all the other animals appeared in excellent condition on day 18, after having received identical doses of cadmium and care.

Figures 11 and 12 illustrate very nicely the high, medium and low elution volumes at which Cd complexes appear. These two figures differ from Figures 2-10 inasmuch as the serum fractions for rat 1 were separated on a 1" x 10" column and collected in 1 ml volumes (320 fractions); the serum fractions for all other animals were separated on a 1" x 5" column (20 ml breakthrough volume) and collected in 5 ml volumes (32 fractions). This was done to decrease the time spent on sample analysis; no significant loss of information was noted due to the slight decrease in resolution. The two separations were U.V. light-treated because the labile-complexed metal appeared only in the intermediate and low molecular weight regions; therefore, ligand destruction was required to see metals present in the large molecular weight regions. The labile and total metal content was one and the same in the low and intermediate molecular weight regions.

Figures 13 and 14 show the large, intermediate, and low molecular weight ligands present in the binding of Pb and Cu respectively. These are presented for comparison with the appropriate binding regions in Figures 3, 4, 6, 7, 9 and 10.

The labile and nonlabile metal complexes for cadmium, lead and copper are very dramatically shown in Figures 15 through 20. In these illustrations one can see the effect of nonlabile metal complexes and realize the need for complete ligand digestion or denaturation prior to analysis. It further demonstrates that nonlabile complexing is primarily a function of large molecular weight serum components, i.e. albumin, globulin, and ceruloplasmin weights.

Another very interesting phenomenon is the shift with time from low and intermediate molecular weight serum components to large molecular weight serum materials by trace metals. Figure 21 gives the distribution of cadmium in a rat 4 serum sample separated on the 1" x 5" column; Figure 22 shows the results of a second aliquot of the same serum sample used for Figure 21. This aliquot was passed through the 1" x 5" column after having been allowed to stand, covered, for 3.5 hours at 56°F - an *in vitro* shift is demonstrated.

An *in vivo* trace metal shift for Cd was demonstrated in rat 2 (Fig. 23) by taking a serum sample 30 minutes after an injection of Cd, and passing 200 µl of the sample through the 1" x 5" column. Five days later another serum sample was collected from the same animal after four days of Cd injection. There was no Cd given on the fifth day. The Cd was found almost exclusively in the large molecular weight fractions of the serum (Figure 24).

It would seem logical, therefore, to conclude that trace metal shifts from low and intermediate molecular weight serum materials to large ones are a normal action based upon rats 2 and 4. It might further indicate that the early demise of rat 1 was the result of the Cd being: (1) in a labile form exclusively, and (2) in intermediate and low molecular weight serum components without the "normal" transfer to the larger materials. The intermediate and low molecular weight materials might very well be trans-cellular membrane transport vehicles due to their sizes. This could mean a large trace metal insult to vital organs over a relatively short period of time (15-30 days), even though the insulting heavy metal levels were "low" and the exposure chronic. Could these complexation states and trace metal distributions be used as a means of determining susceptibles in an animal population?

The red blood cell (RBC) pictures that coincide with the serum samples for animals 2-4 are found in Figures 25 through 28. The trace metal data is presented in ratio form for ease of study. The microampere ratios are nothing more than the peak heights for Cd in microamperes divided by the peak heights for Pb in microamperes, etc. The peak height of a metal analyzed by ASV is directly related to concentration.

The interesting phenomenon in the RBC work was the way in which the membrane copper concentration changes closely followed the cadmium membrane concentration changes. Lead was of no great interest because it remained low and fairly constant. No explanation is given for the RBC copper response with time and cadmium insult, because no plasible explanation has been found. This is truly an area for further trace metal research, particularly from the interaction standpoint.

In conclusion, one might do well to consider the state of a metal complex -- labile and/or nonlabile -- as well as the quantity of a given metal in a given series of serum component molecular weight distributions, when trying to determine the effects of "low" level long-time trace metal exposures. It is also possible that the foregoing line of investigation is capable of revealing the heavy metal poisoning susceptibles in a population -- an interesting thought. If this is true, or if such an approach indicates early signs of a biological response to heavy metal insult, the procedure might prove useful in the establishing of atmospheric and industrial heavy metal concentration standards. It might also prove valuable in the placement of employees in heavy-metal utilizing industries.

Some insight into the effects of heavy metals on the immune response system of animals has been given by Dr. Ronald Jones, at the University of Michigan, who has been working on the effects of cadmium on the immune response system of rats. To date he has found that a 0.6 mg Cd/Kgm of body weight dose of cadmium chloride, given two weeks prior to an antigenic insult, gives an elevated primary response to the antigen. If the cadmium is given one week prior to the antigenic stimulation, the primary and secondary responses to the antigen are greatly reduced, and for a prolonged period of time. If an antigenic stimulation is given prior to cadmium exposure, there is no primary or secondary immune response reduction or enhancement (from normal) to further stimulation by the same antigen.

This indicates another possible effect of environmental heavy metal concentrations upon man. Depending upon the time, extent and level of exposure, man could find himself more receptive or resistant to Asian flu, the common cold, and other general illnesses. Therefore, the study and understanding of trace metal routes, rates and reservoirs in both the environment and man are of the utmost importance.

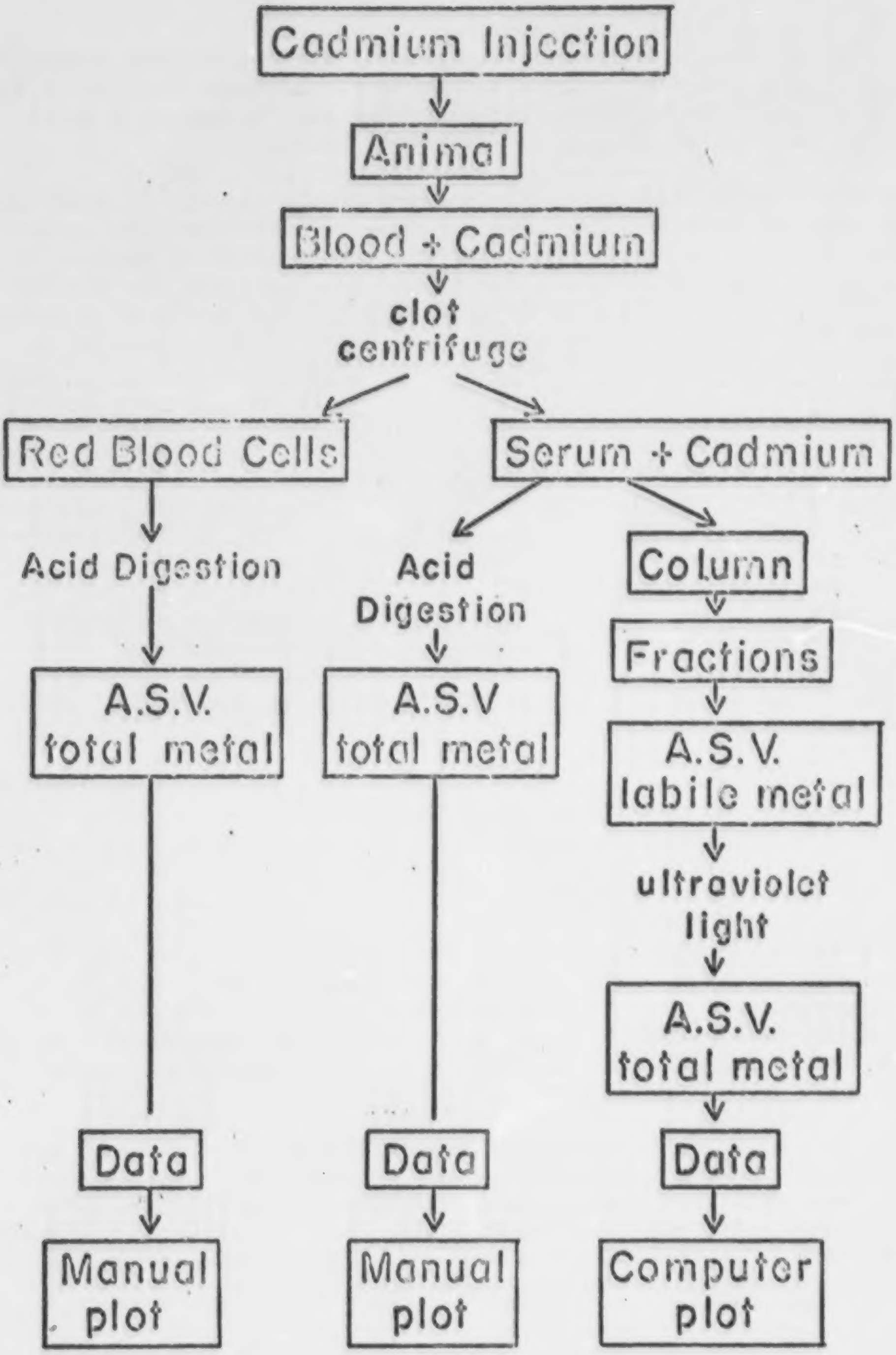

Cadmium Injection
Animal
Blood + Cadmium
clot
centrifuge
Red Blood Cells
Serum + Cadmium
Acid Digestion
Acid
Digestion
Column
Fractions
A.S.V.
total metal
A.S.V
total metal
A.S.V.
labile metal
ultraviolet
light
A.S.V.
total metal
Data
Data
Data
Manual
plot
Manual
plot
Computer
plot

Figure 1. Flow diagram *in vivo* work

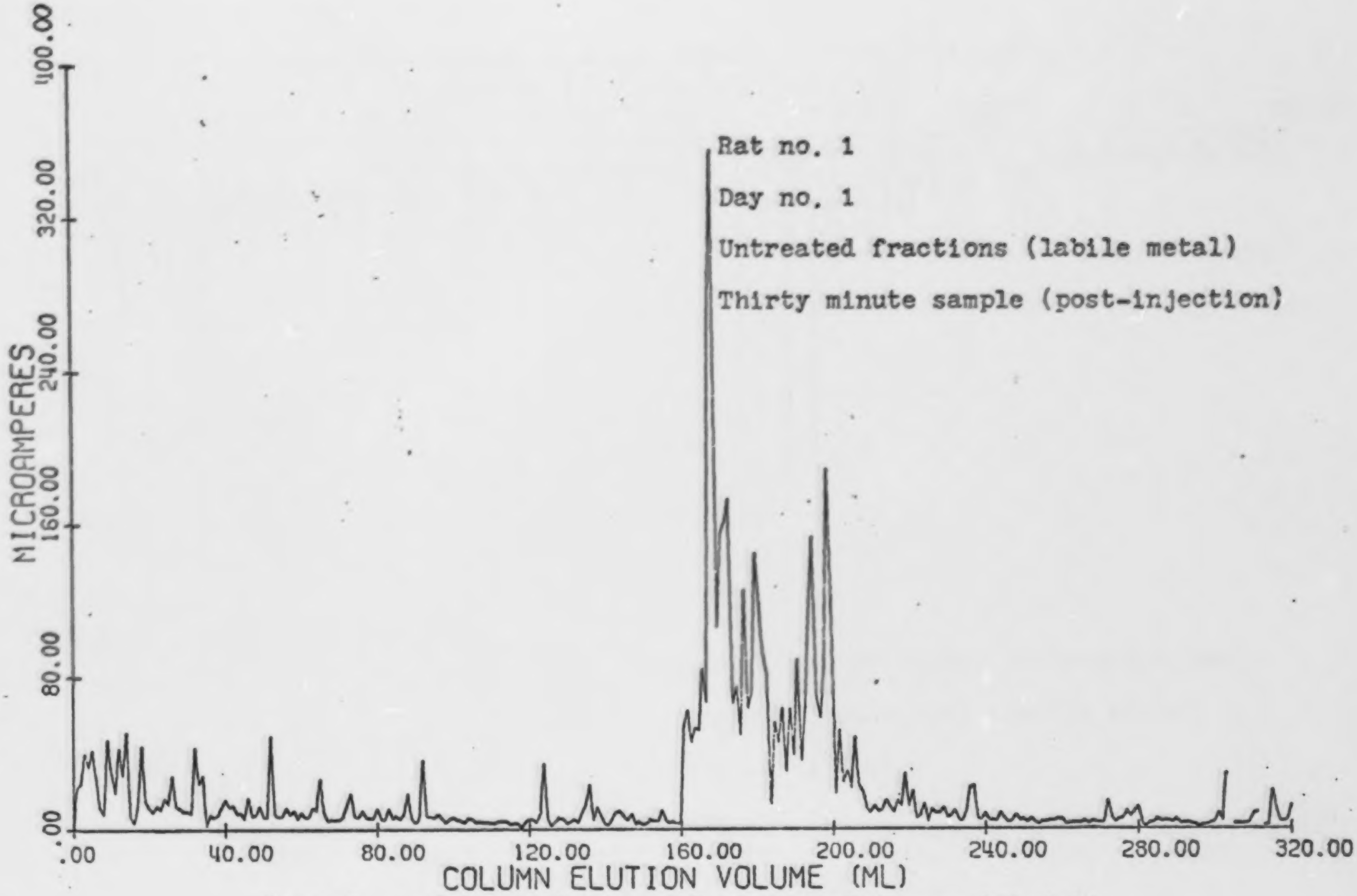


Figure 2. -- Column elution volume vs cadmium peak height

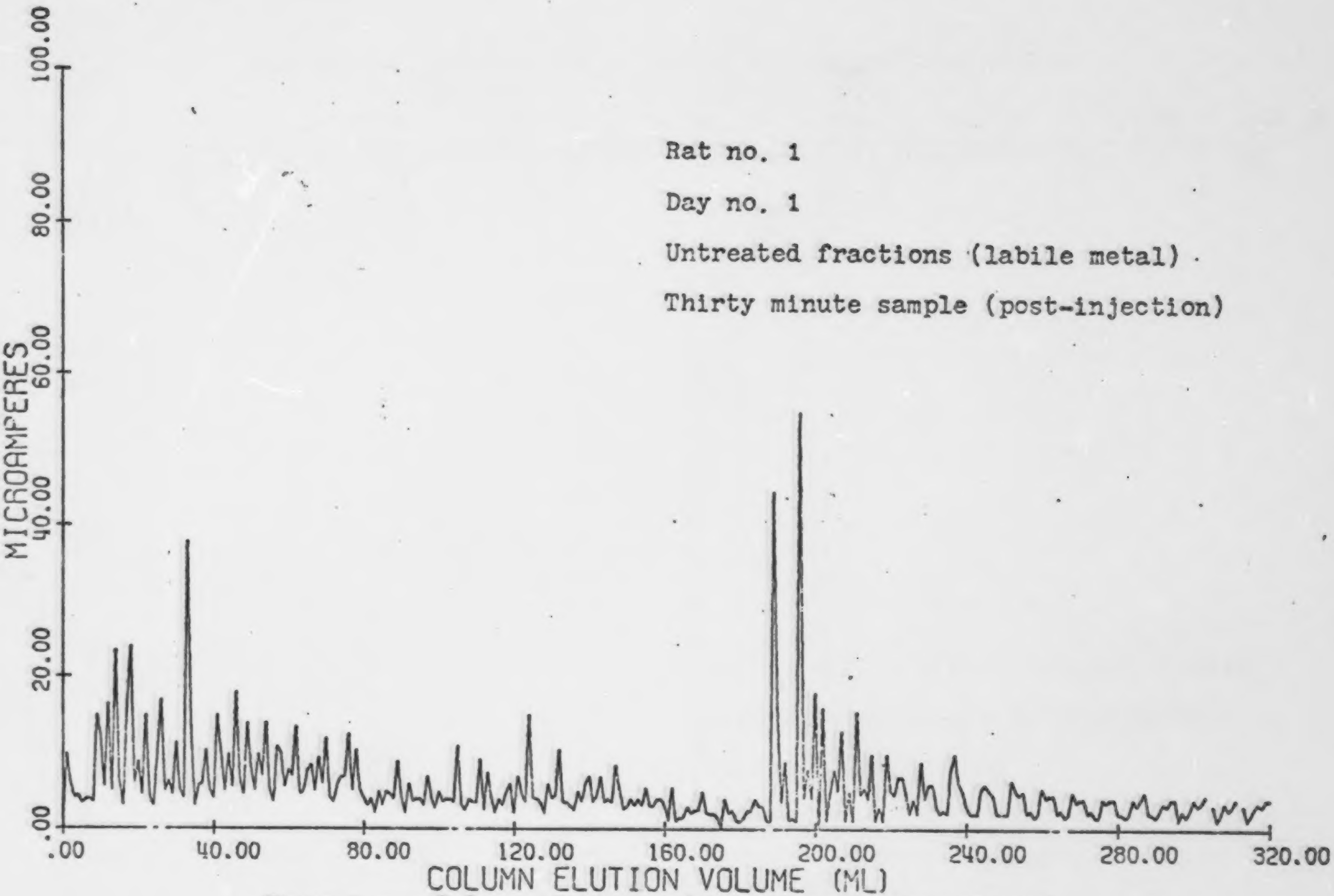


Figure 3. -- Column elution volume vs lead peak height

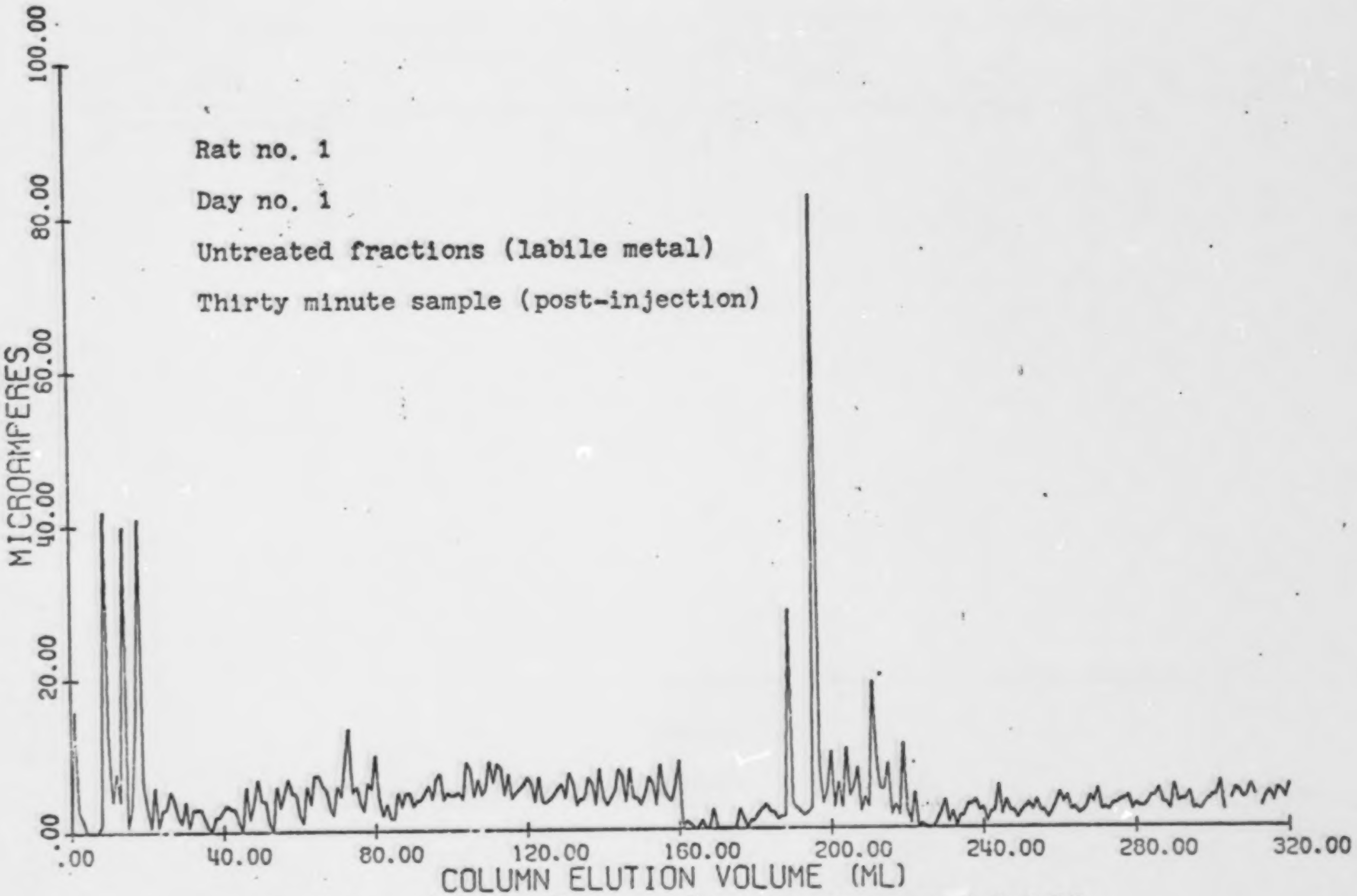
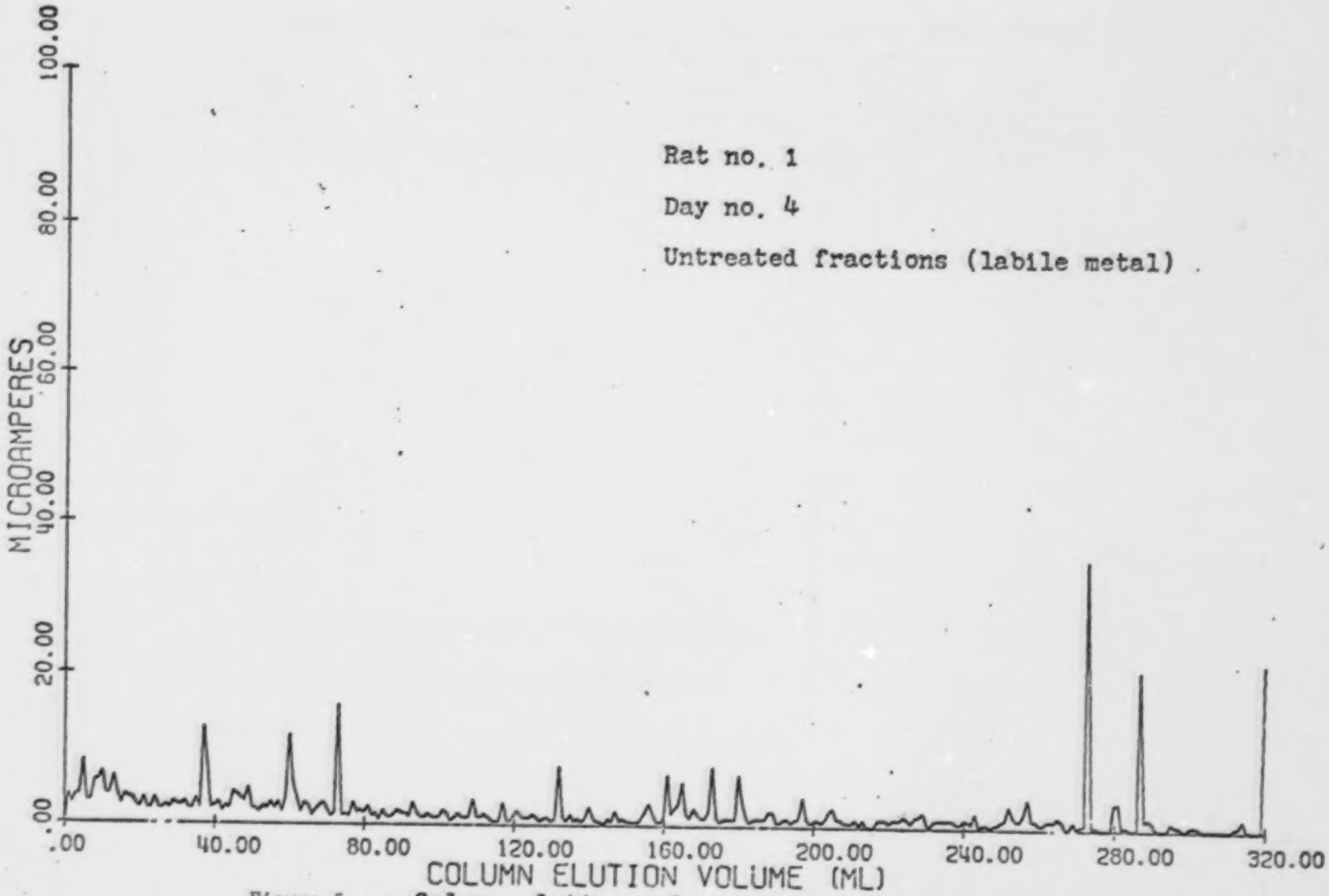


Figure 4. -- Column elution volume vs copper peak height

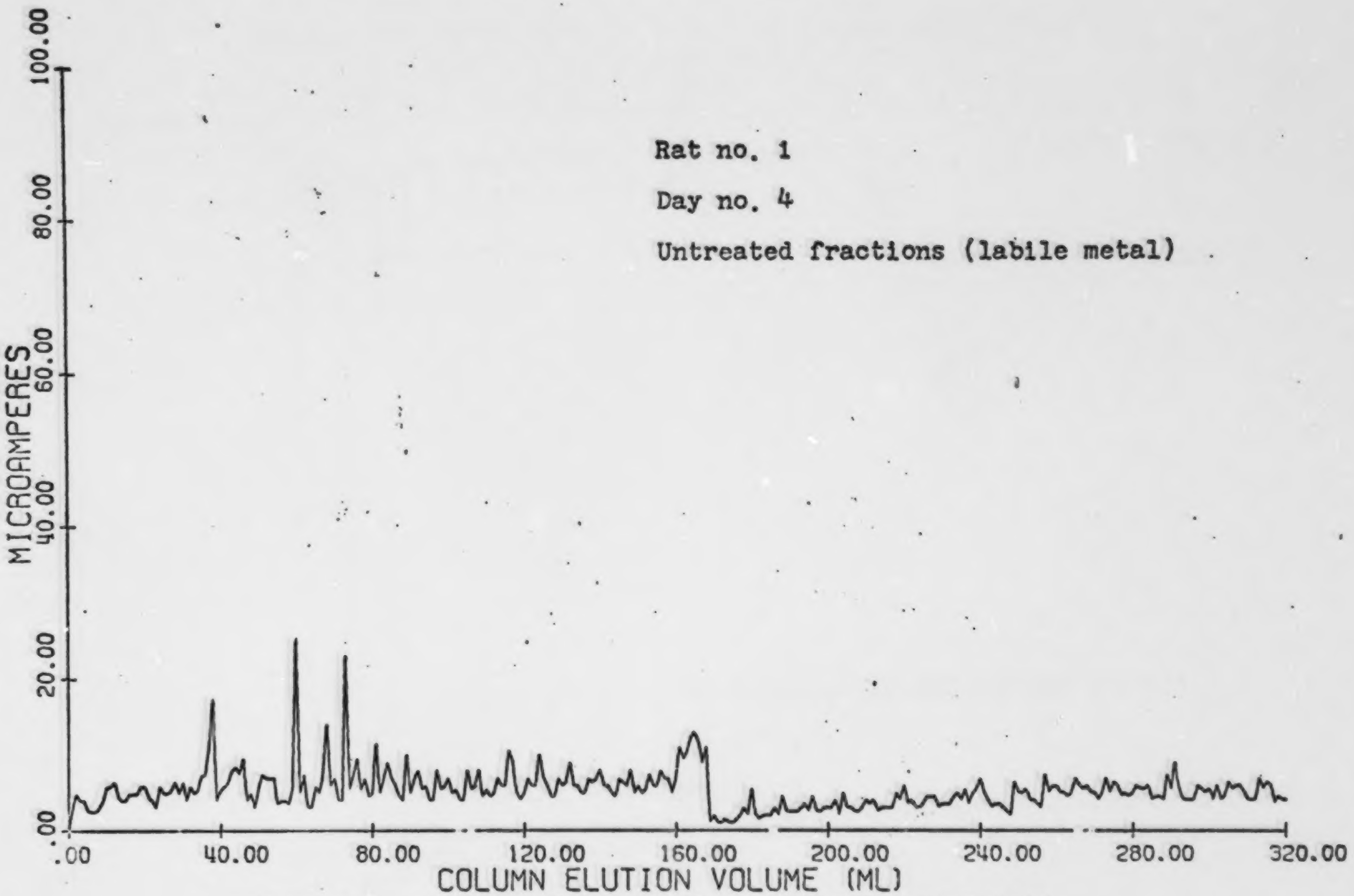


Rat no. 1

Day no. 4

Untreated fractions (labile metal)

Figure 5. -- Column elution volume vs cadmium peak height



Rat no. 1

Day no. 4

Untreated fractions (labile metal)

Figure 6. -- Column elution volume vs lead peak height

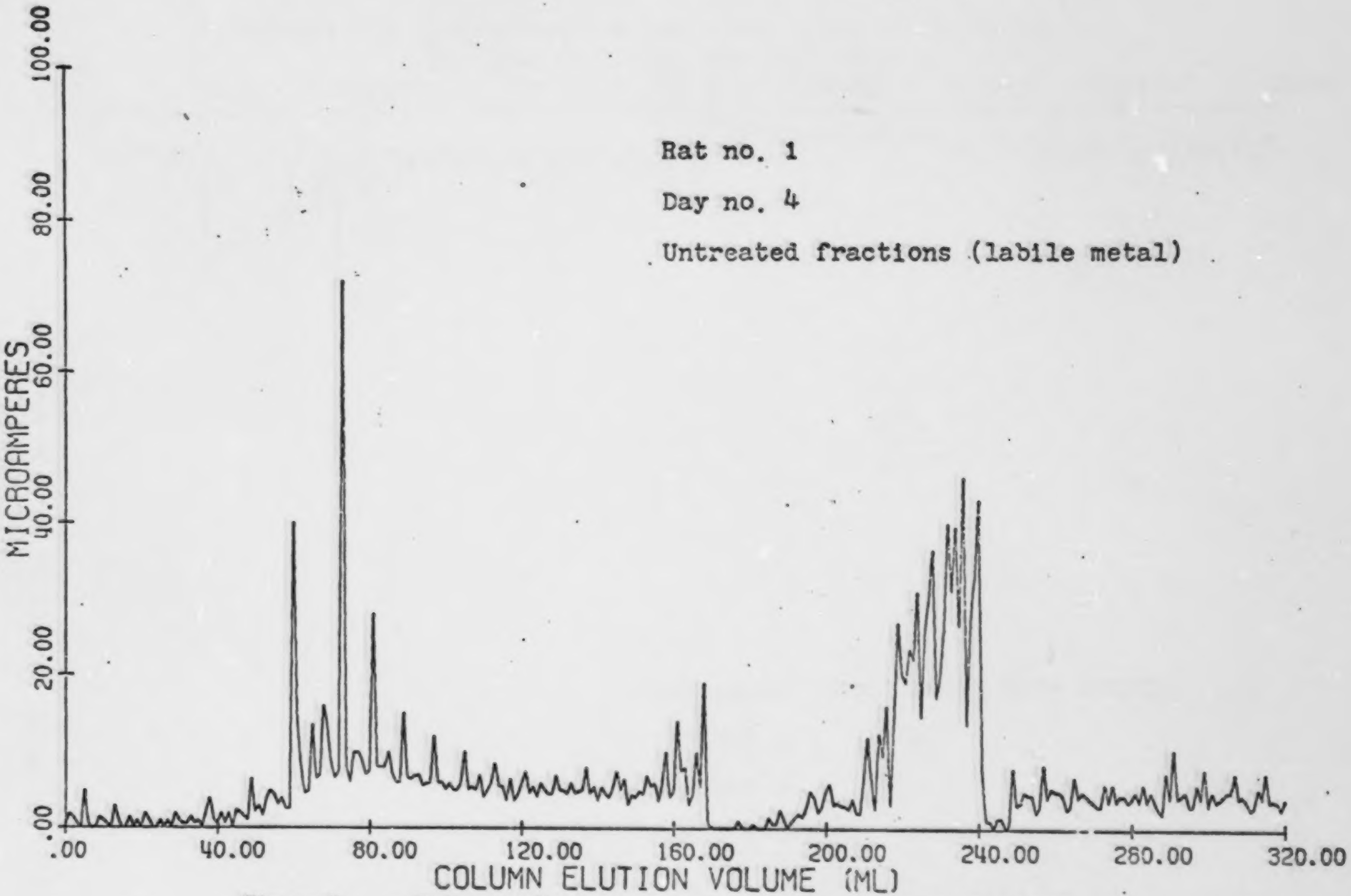


Figure 7. -- Column elution volume vs copper peak height

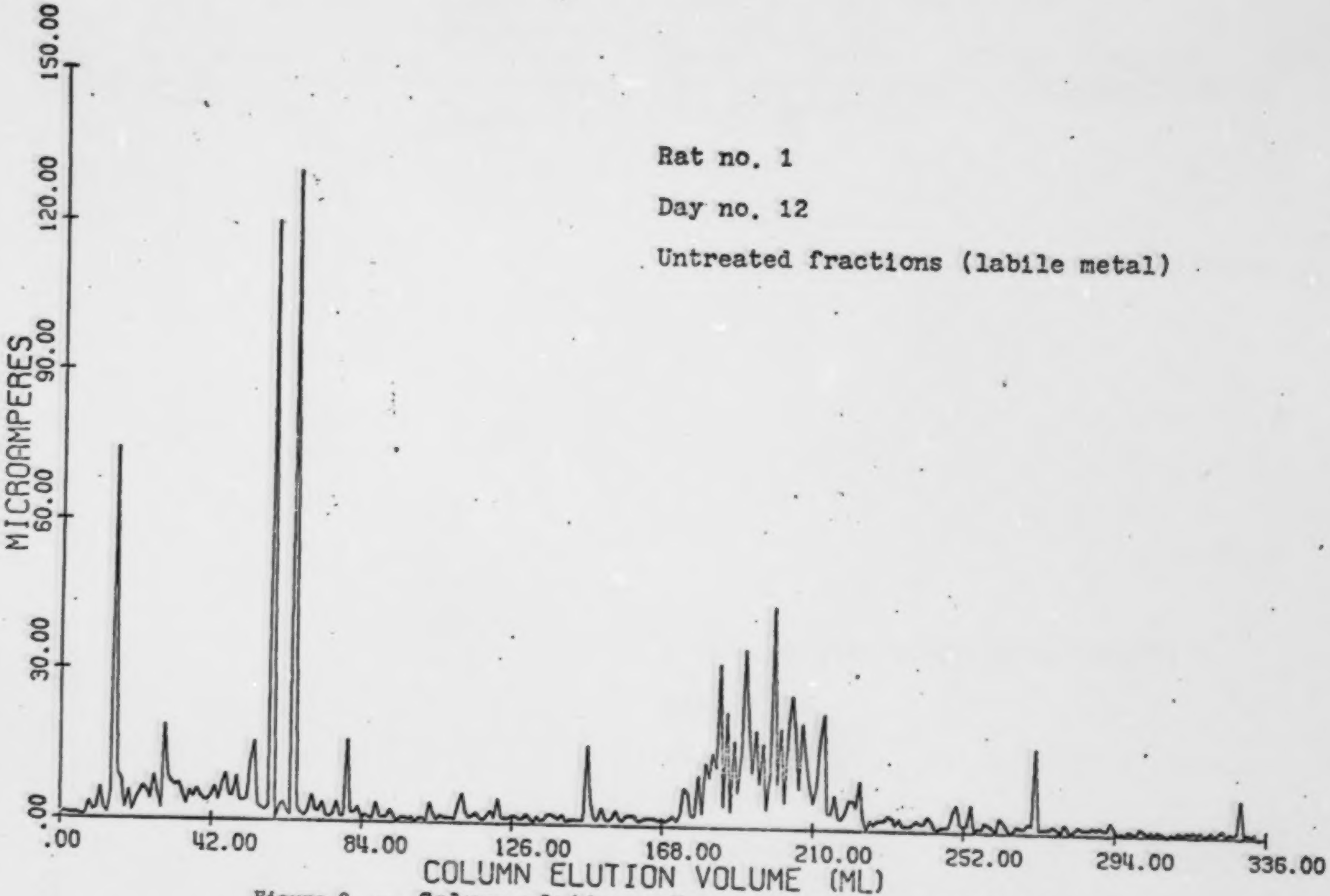
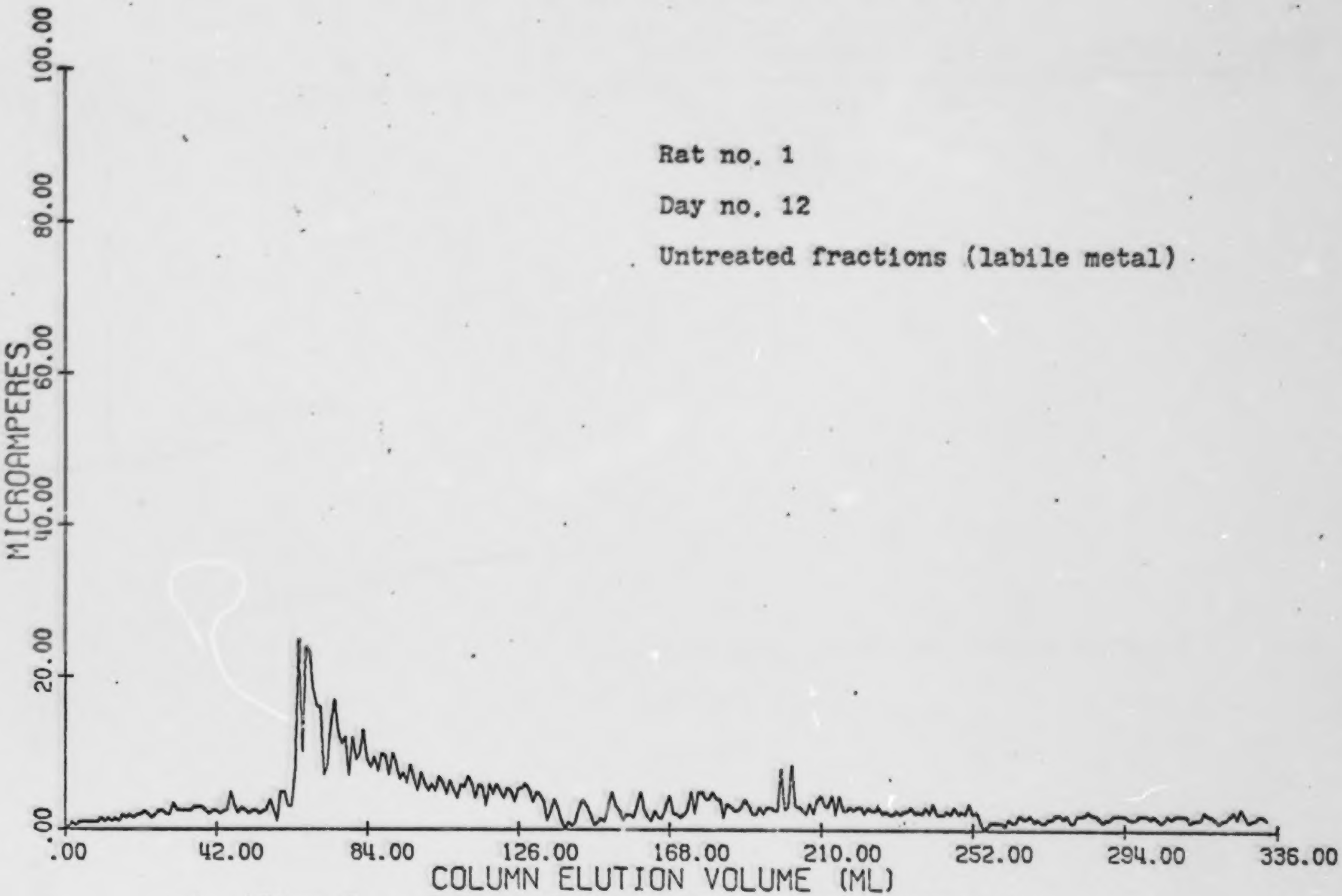


Figure 8. -- Column elution volume vs cadmium peak height



Rat no. 1

Day no. 12

Untreated fractions (labile metal)

Figure 9. -- Column elution volume vs lead peak height

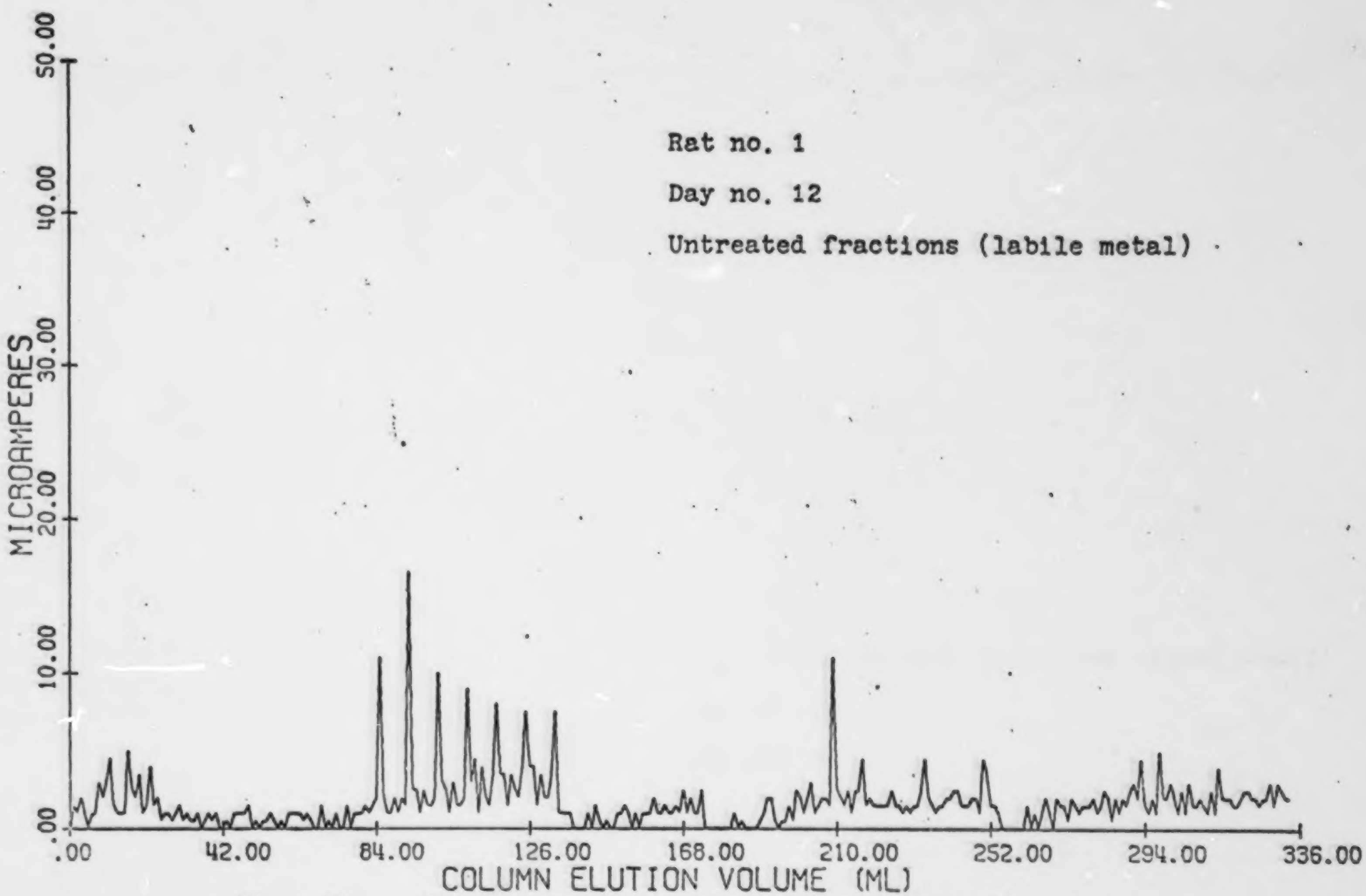
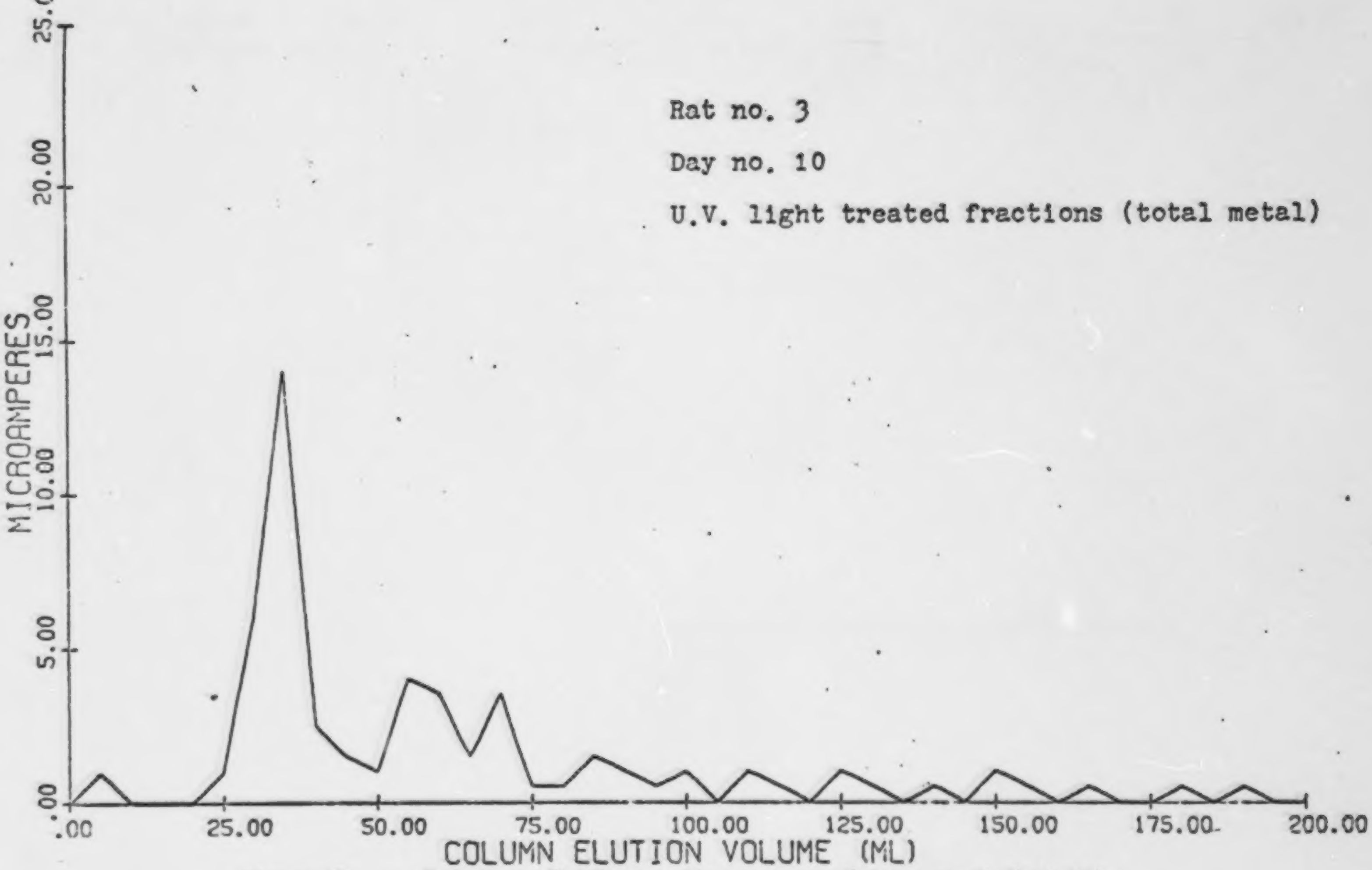


Figure 10. -- Column elution volume vs copper peak height



Rat no. 3

Day no. 10

U.V. light treated fractions (total metal)

Figure 11. — Column elution volume vs cadmium peak height

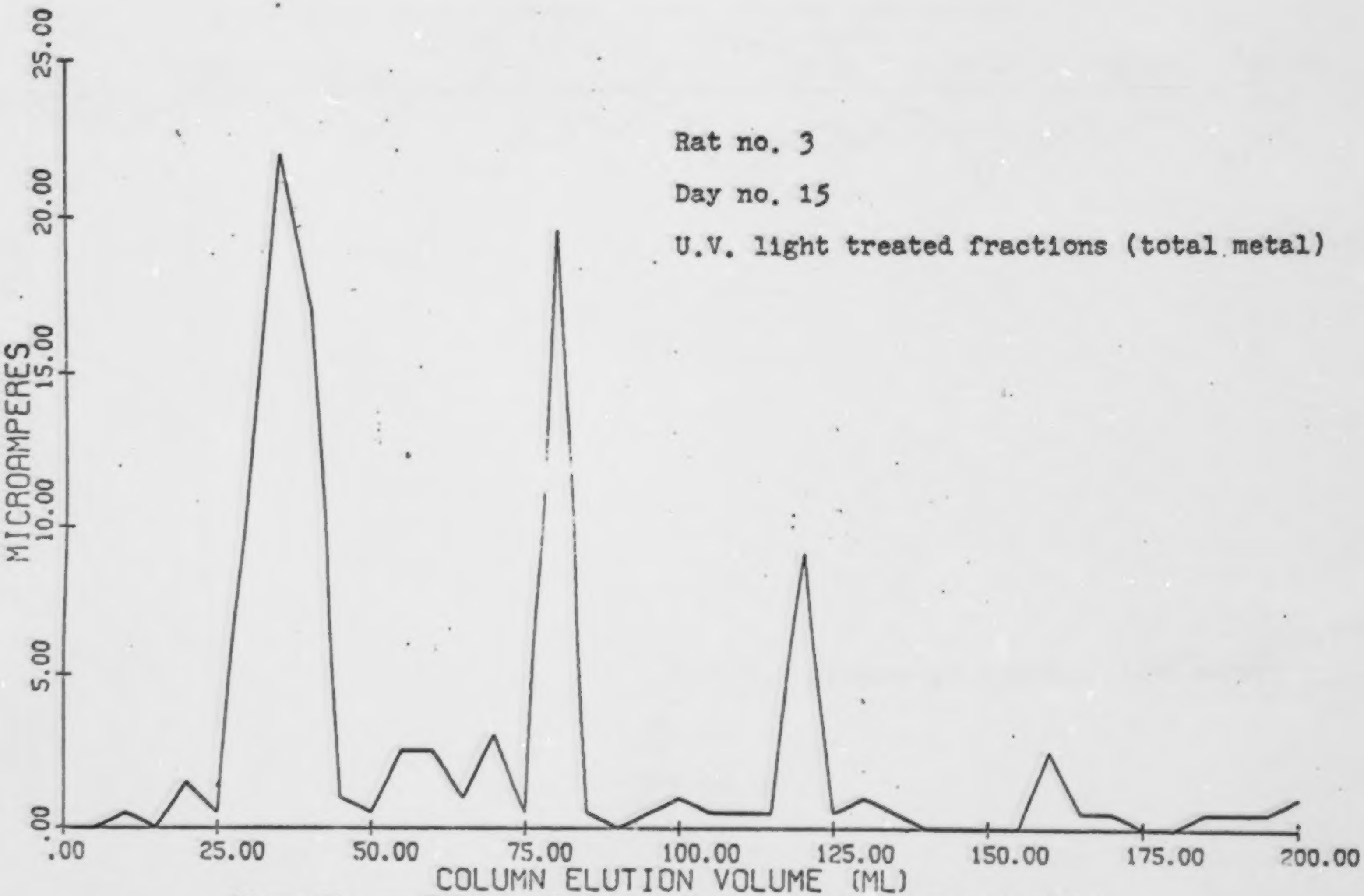


Figure 12. -- Column elution volume vs cadmium peak height

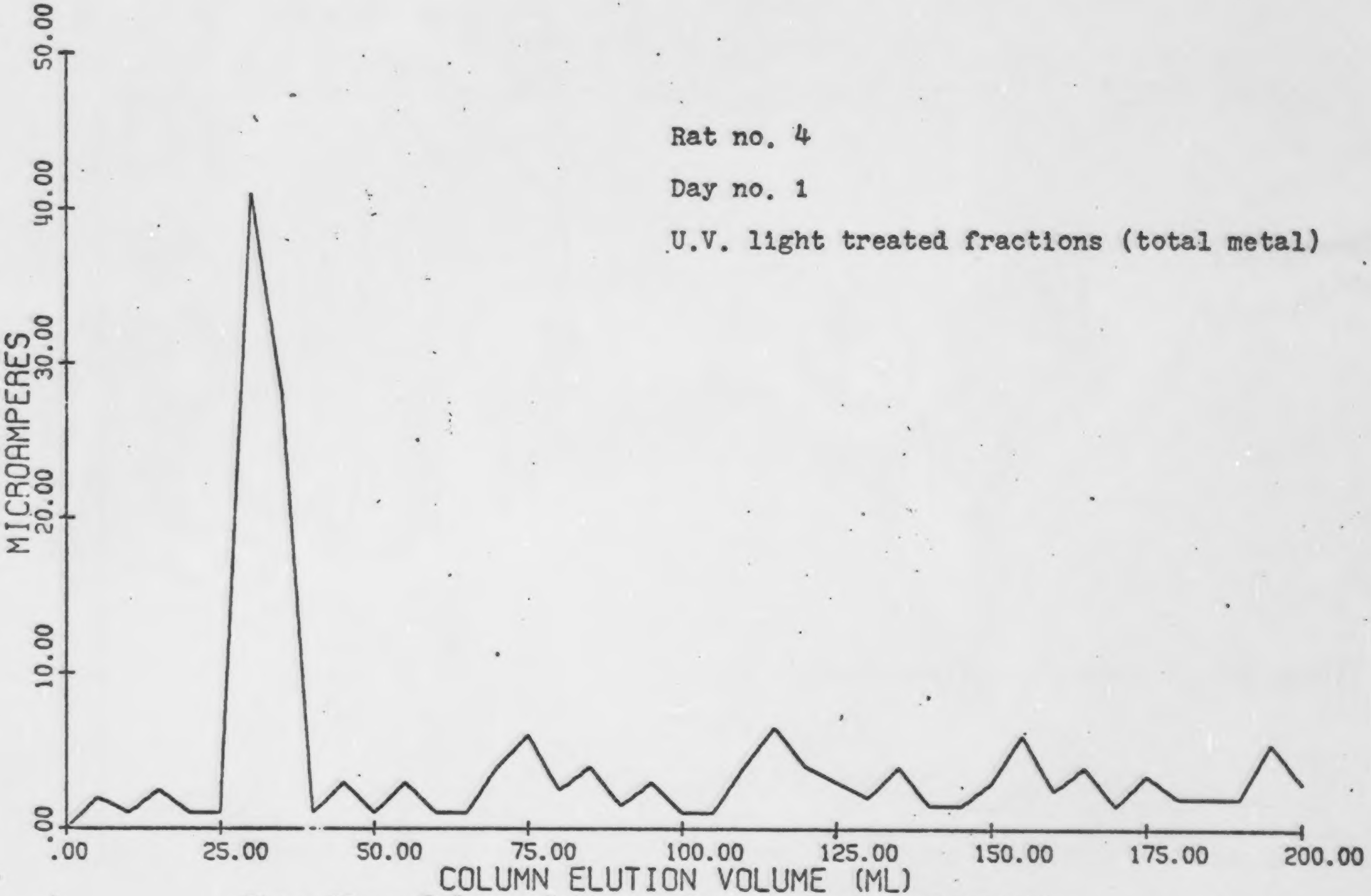


Figure 13. -- Column elution volume vs lead peak height

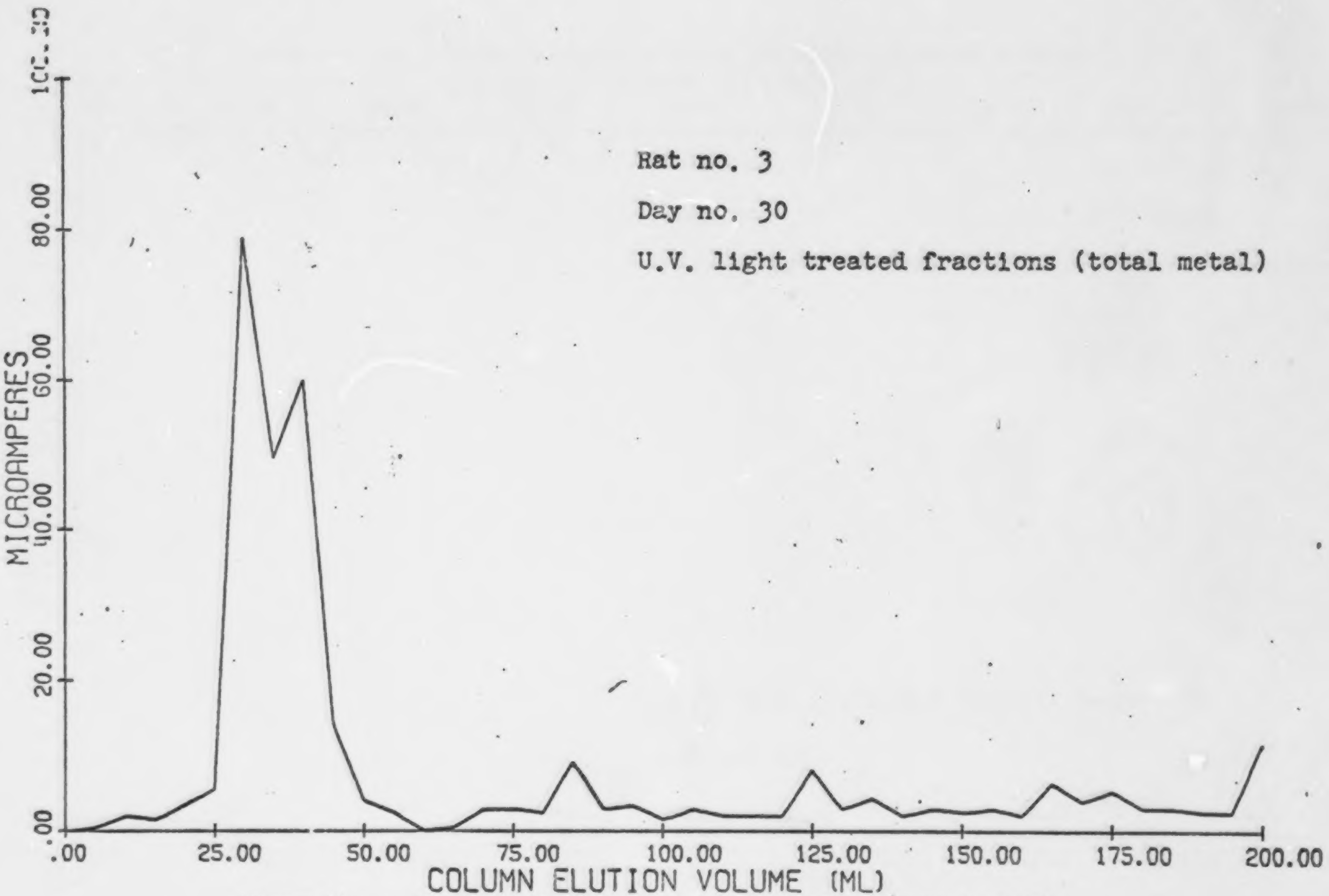


Figure 14. -- Column elution volume vs copper peak height

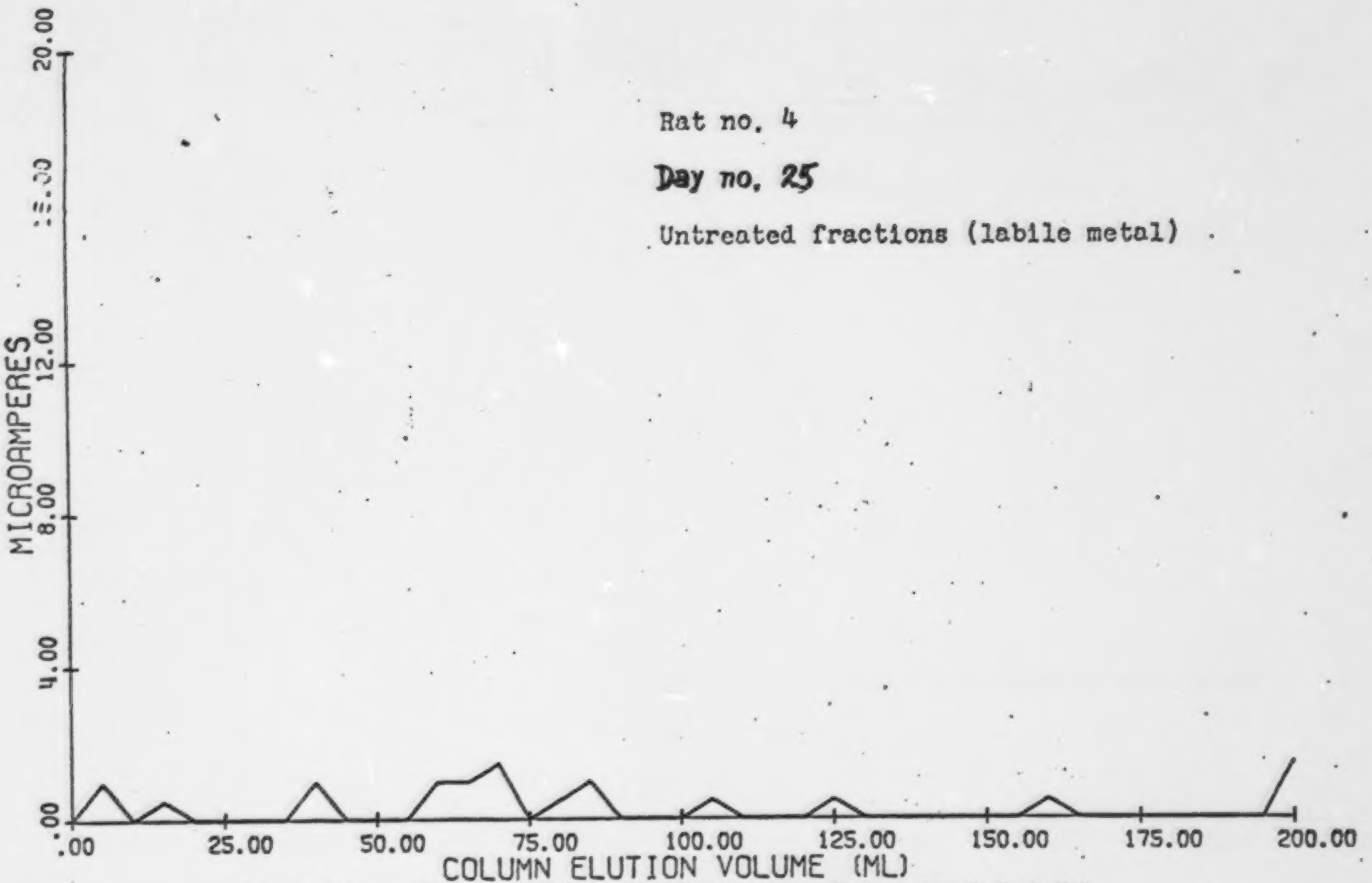


Figure 15. -- Column elution volume vs cadmium peak height

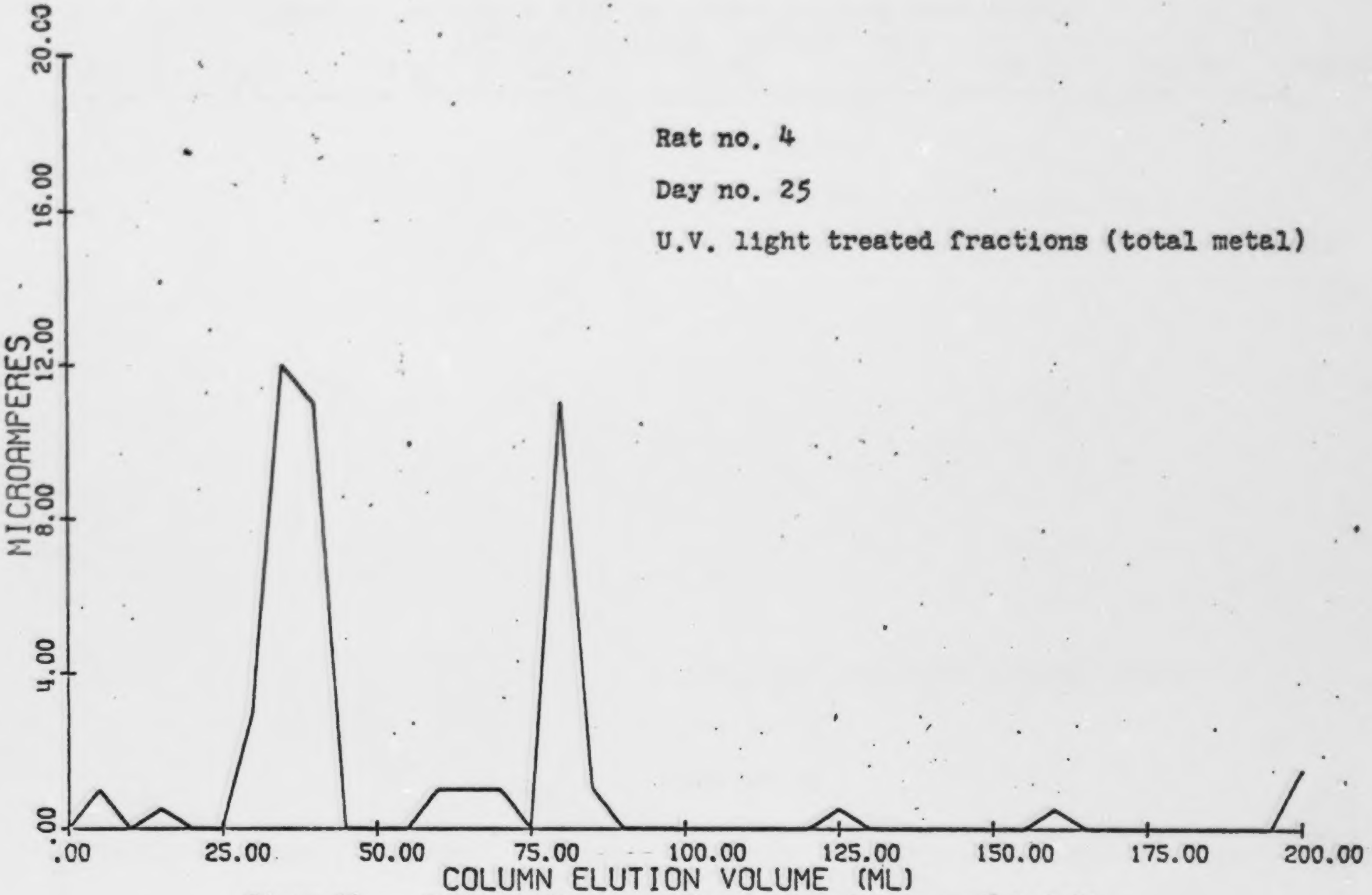


Figure 16. -- Column elution volume vs cadmium peak height

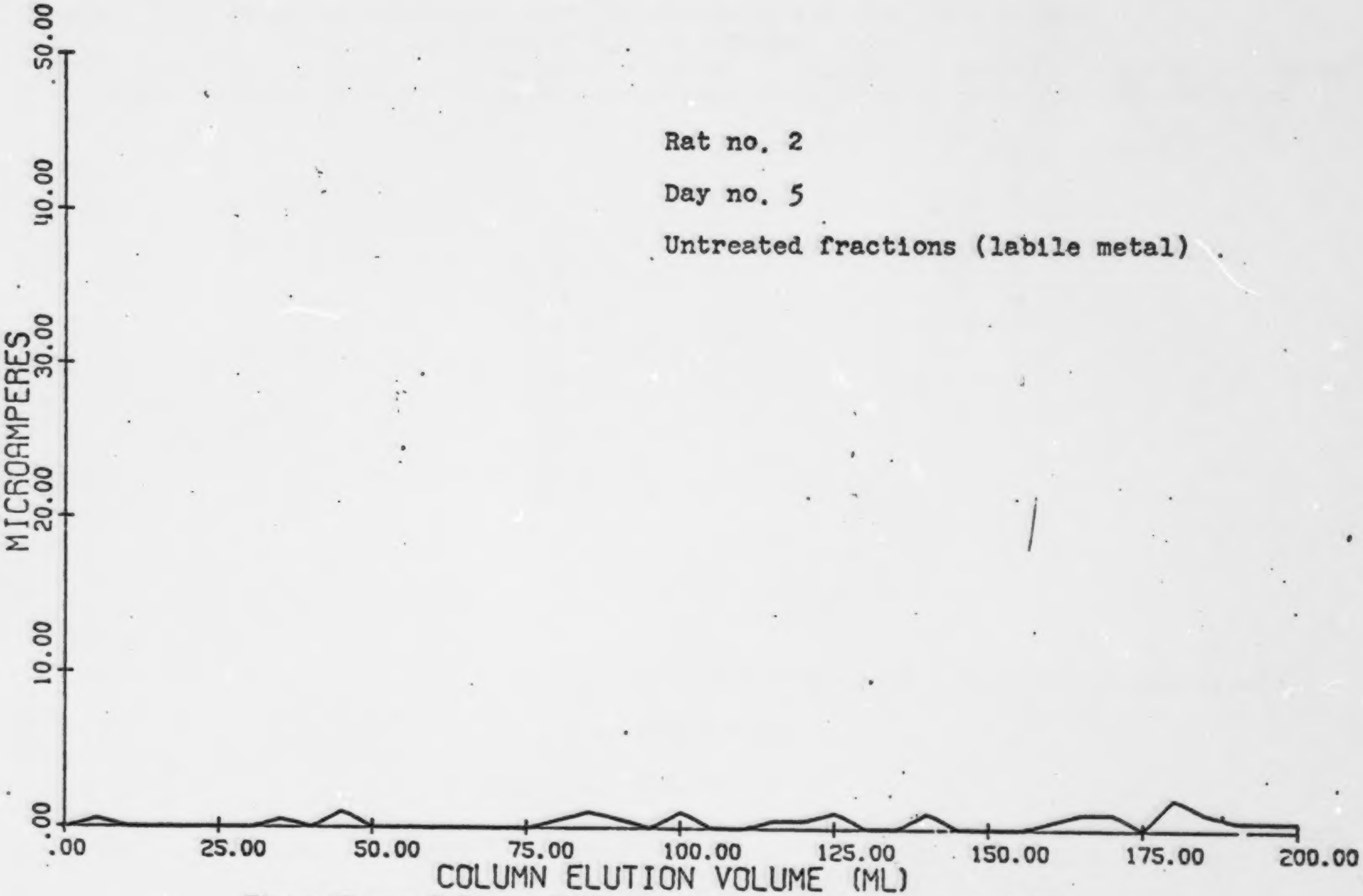


Figure 17. -- Column elution volume vs lead peak height

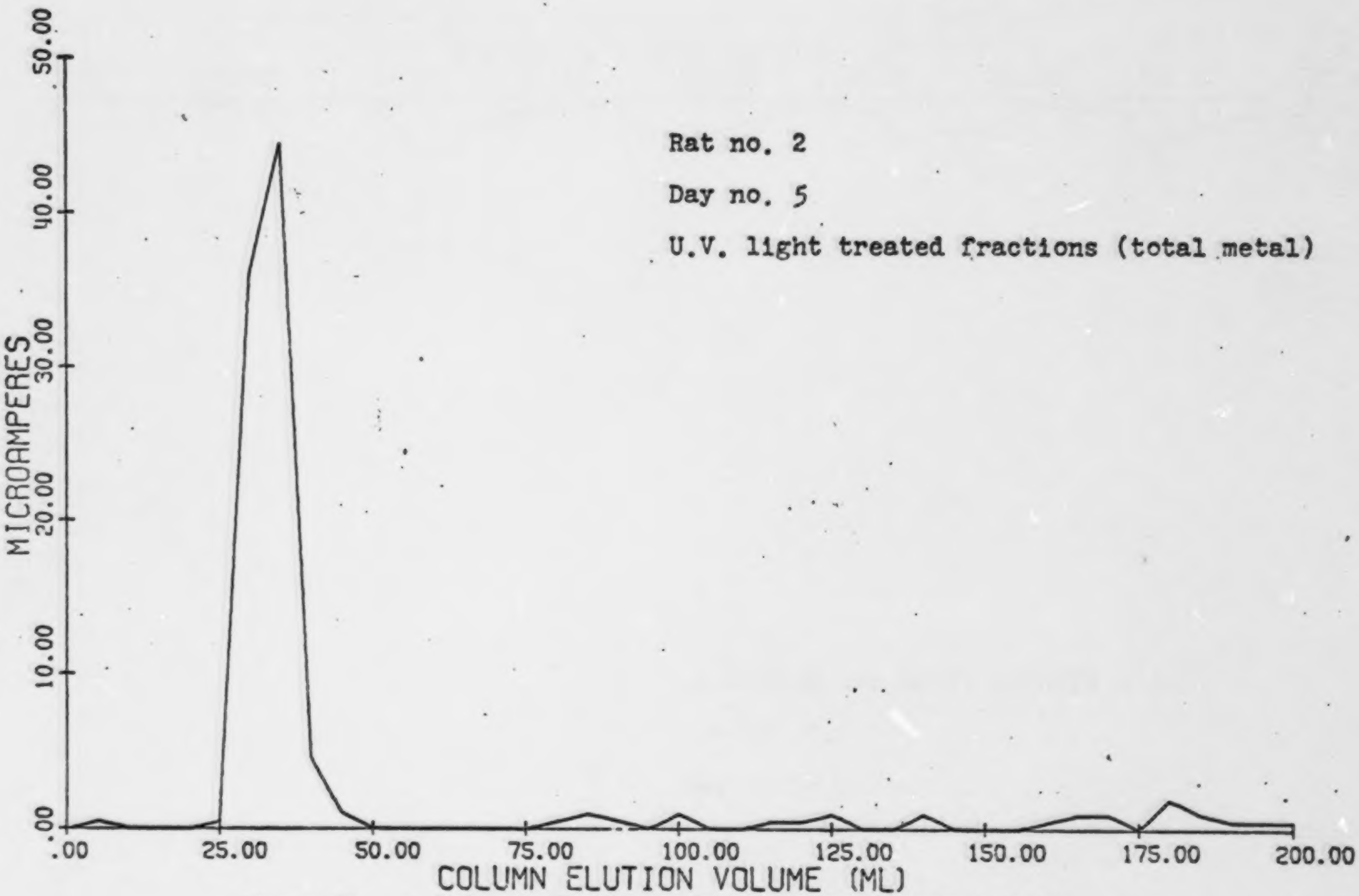


Figure 18. -- Column elution volume vs lead peak height

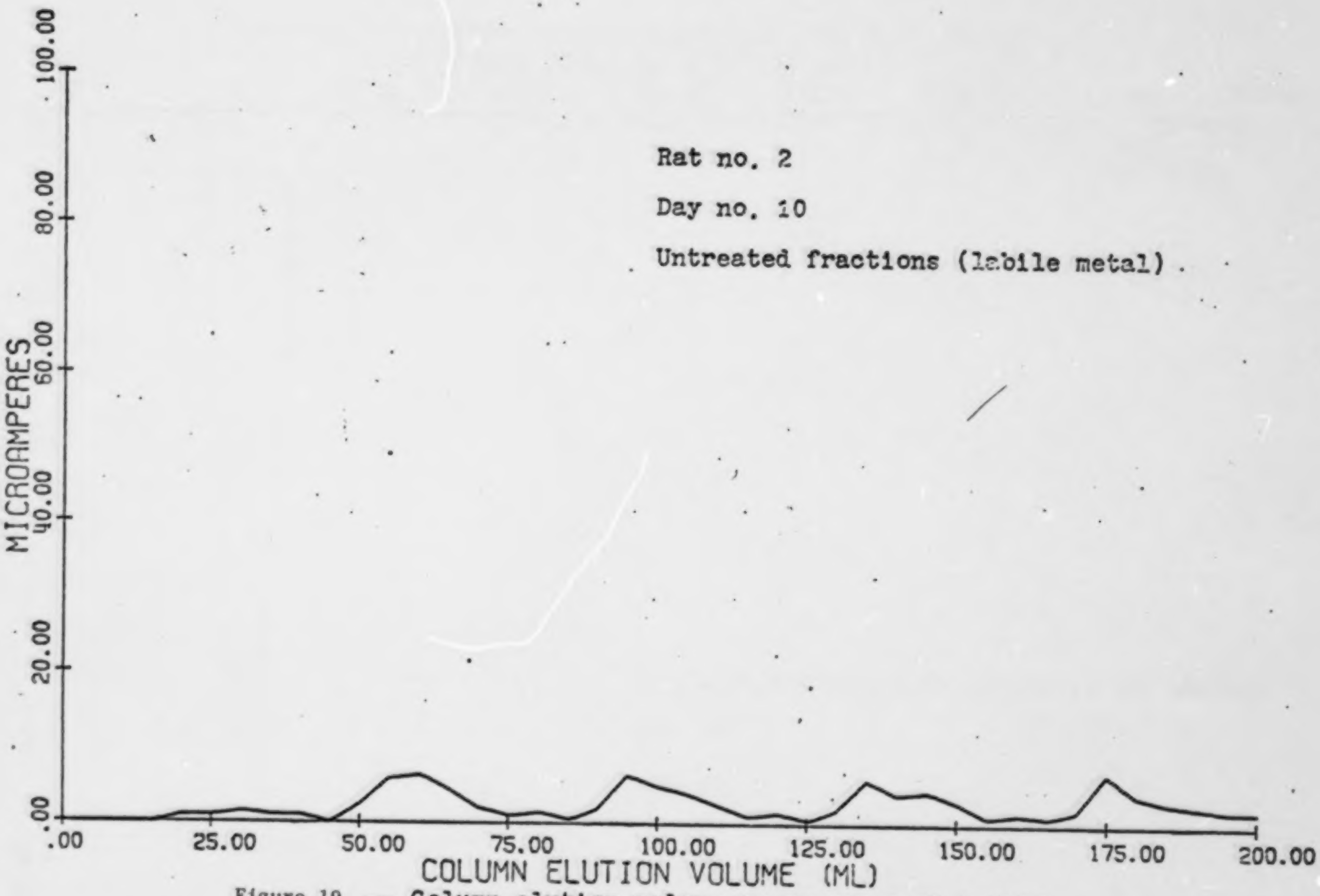
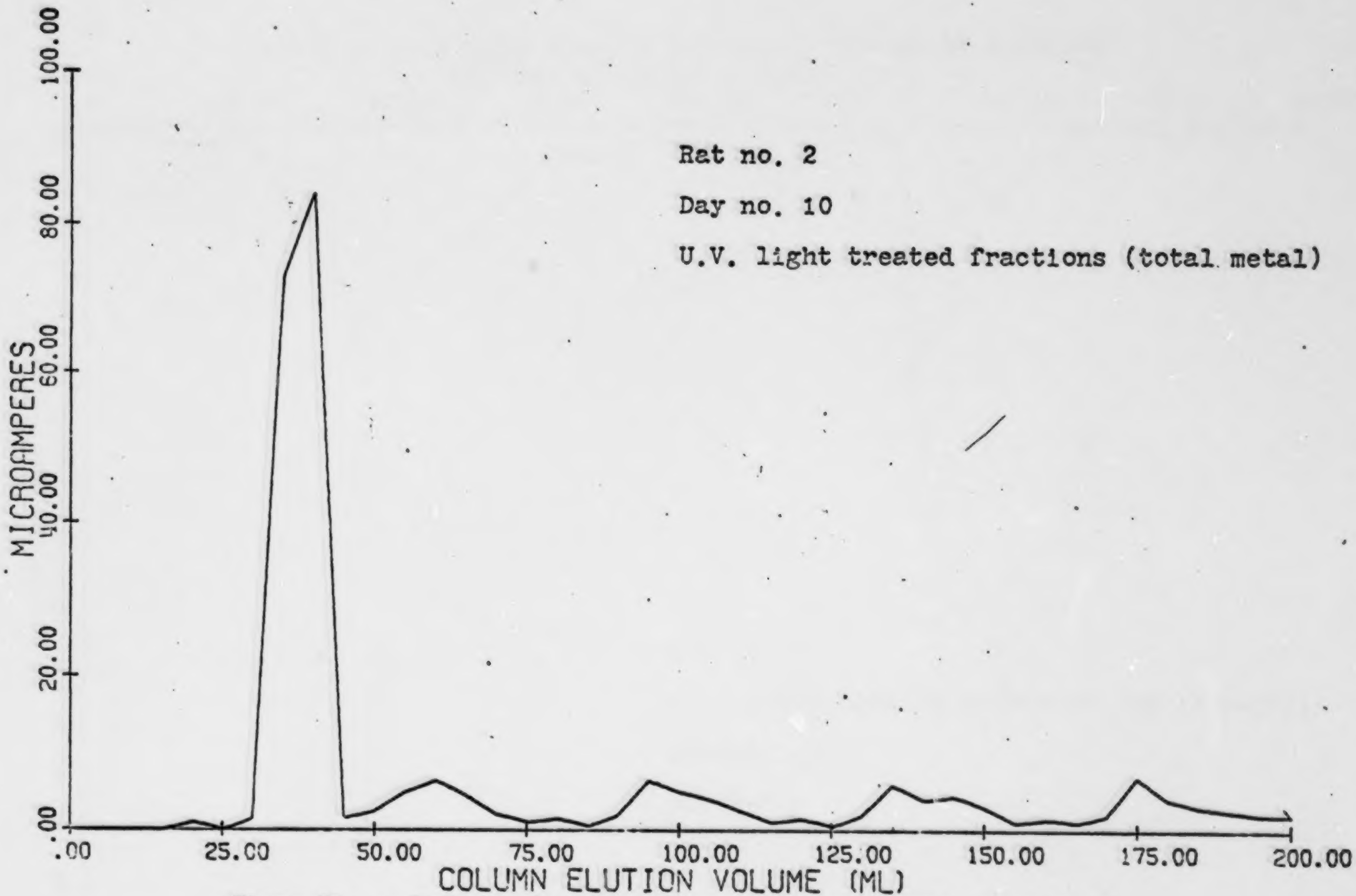


Figure 19. -- Column elution volume vs copper peak height



Rat no. 2

Day no. 10

U.V. light treated fractions (total metal)

Figure 20. -- Column elution volume vs copper peak height

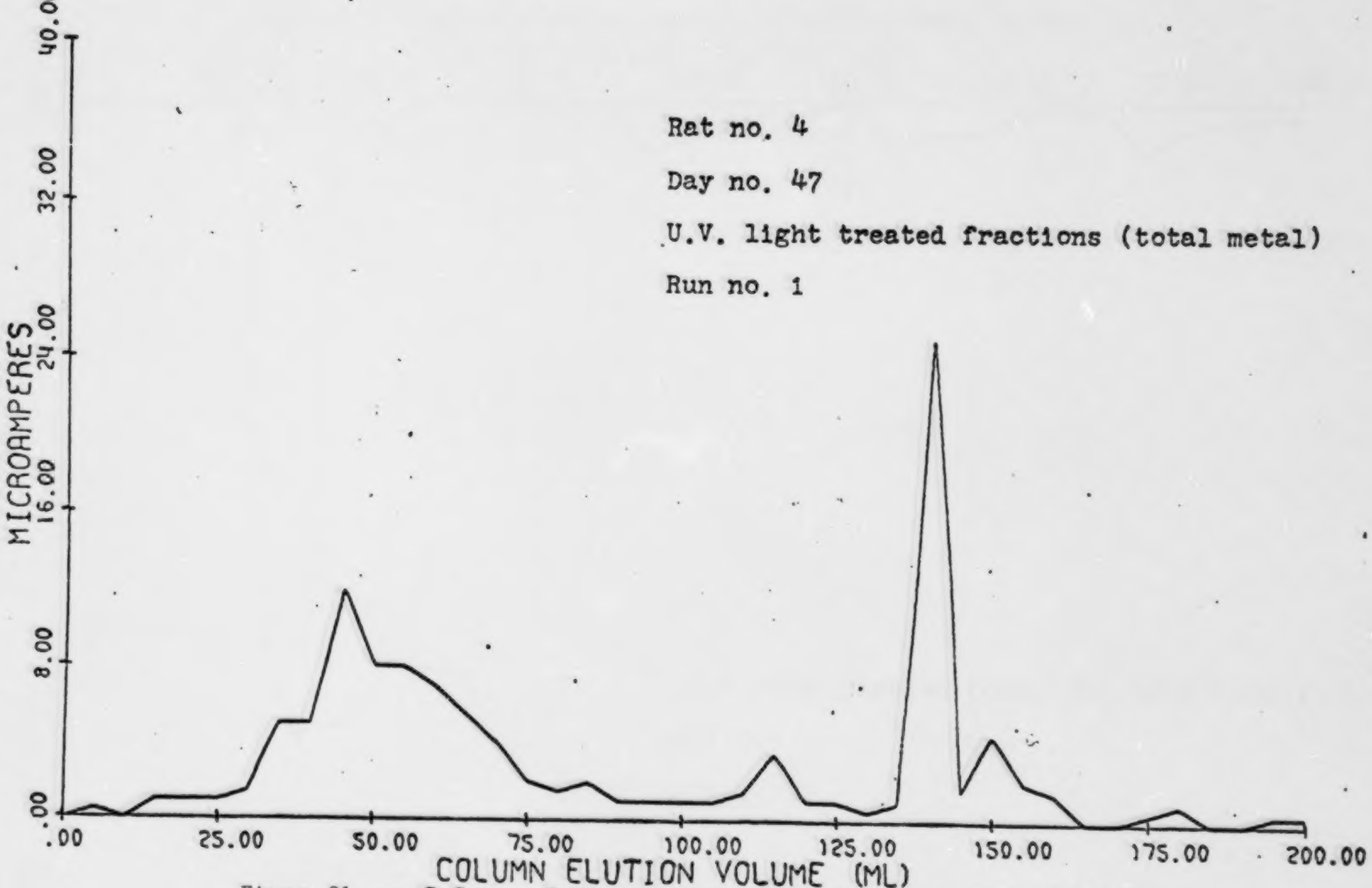
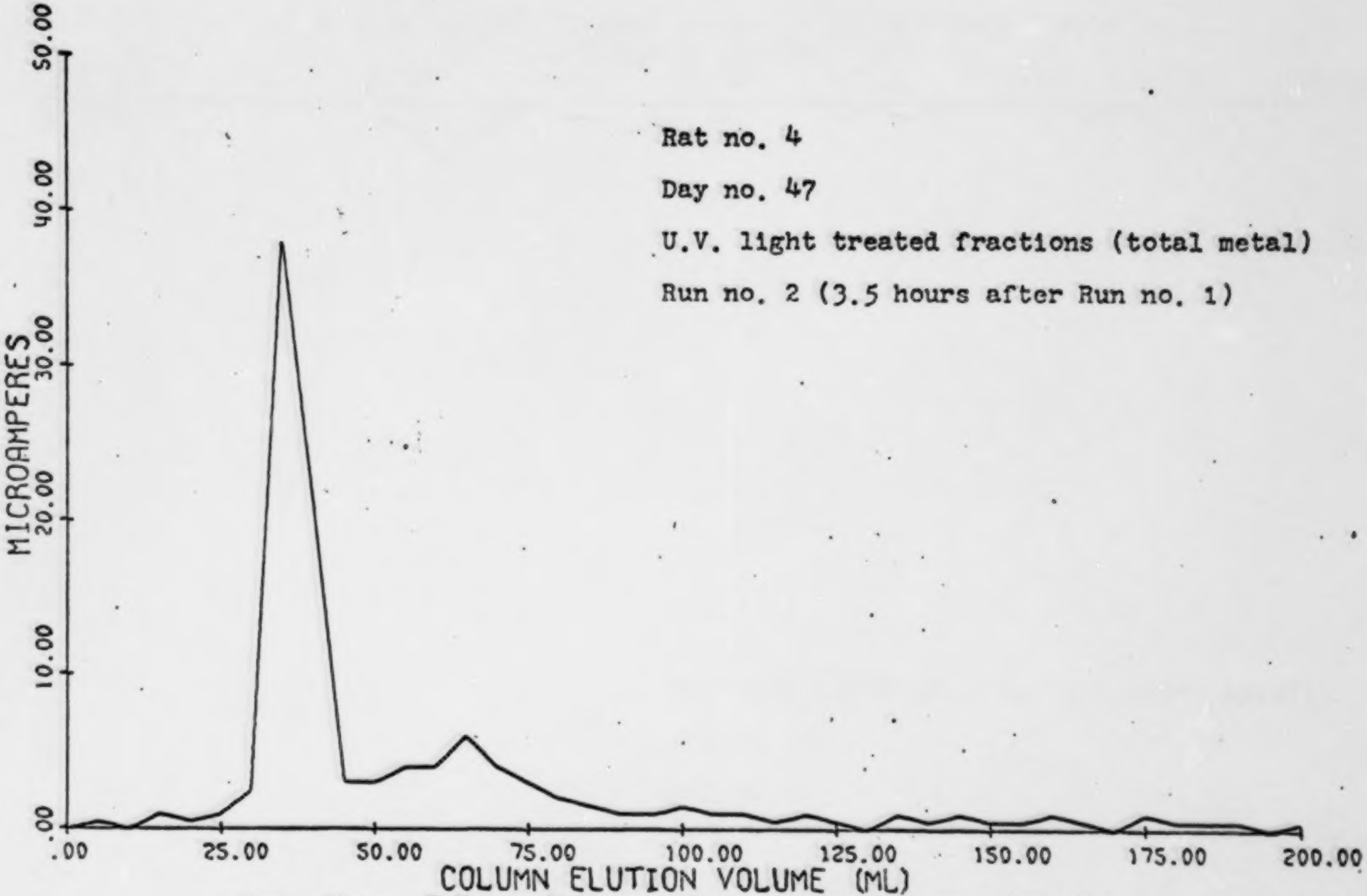


Figure 21. -- Column elution volume vs cadmium peak height



Rat no. 4

Day no. 47

U.V. light treated fractions (total metal)

Run no. 2 (3.5 hours after Run no. 1)

Figure 22. -- Column elution volume vs cadmium peak height

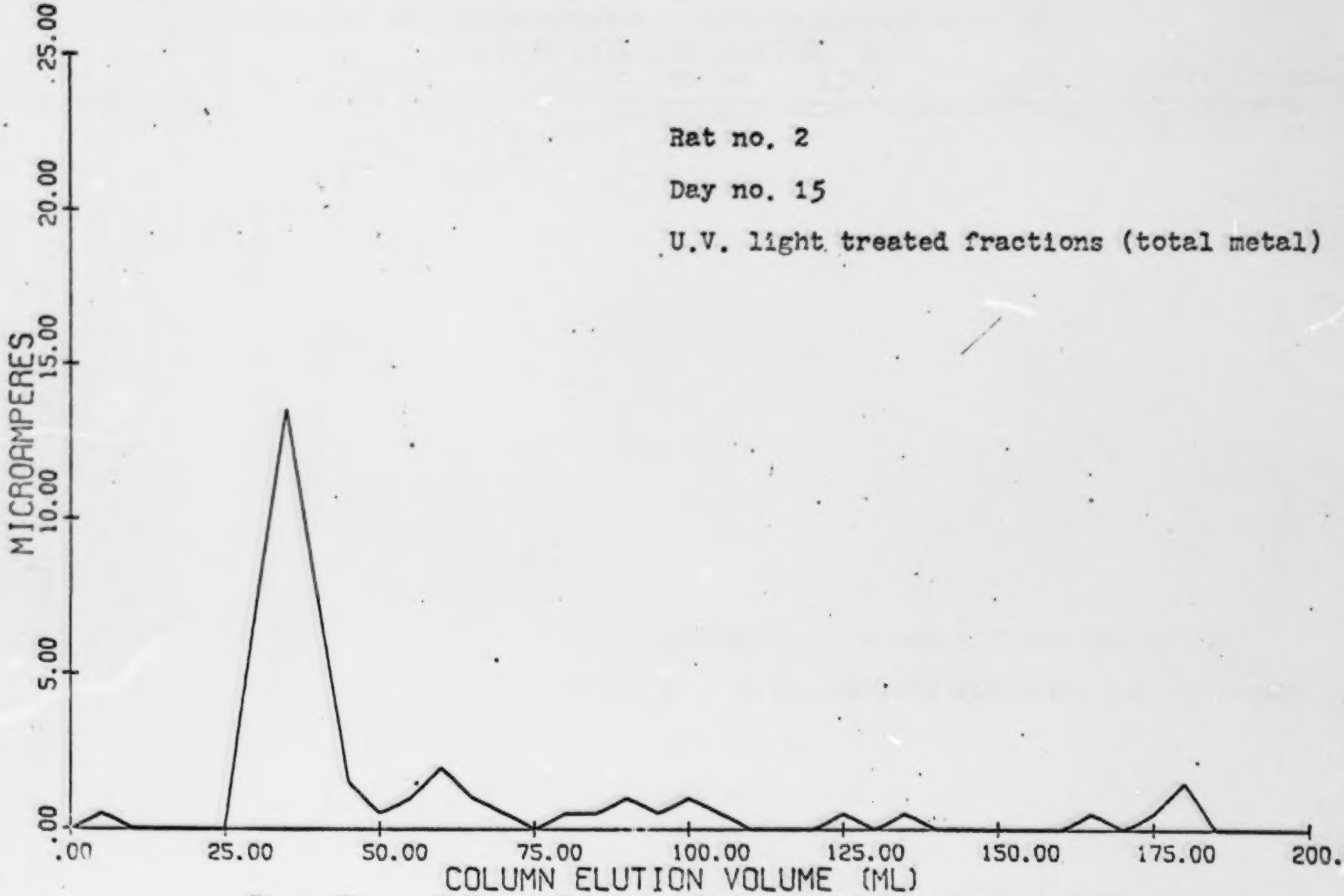
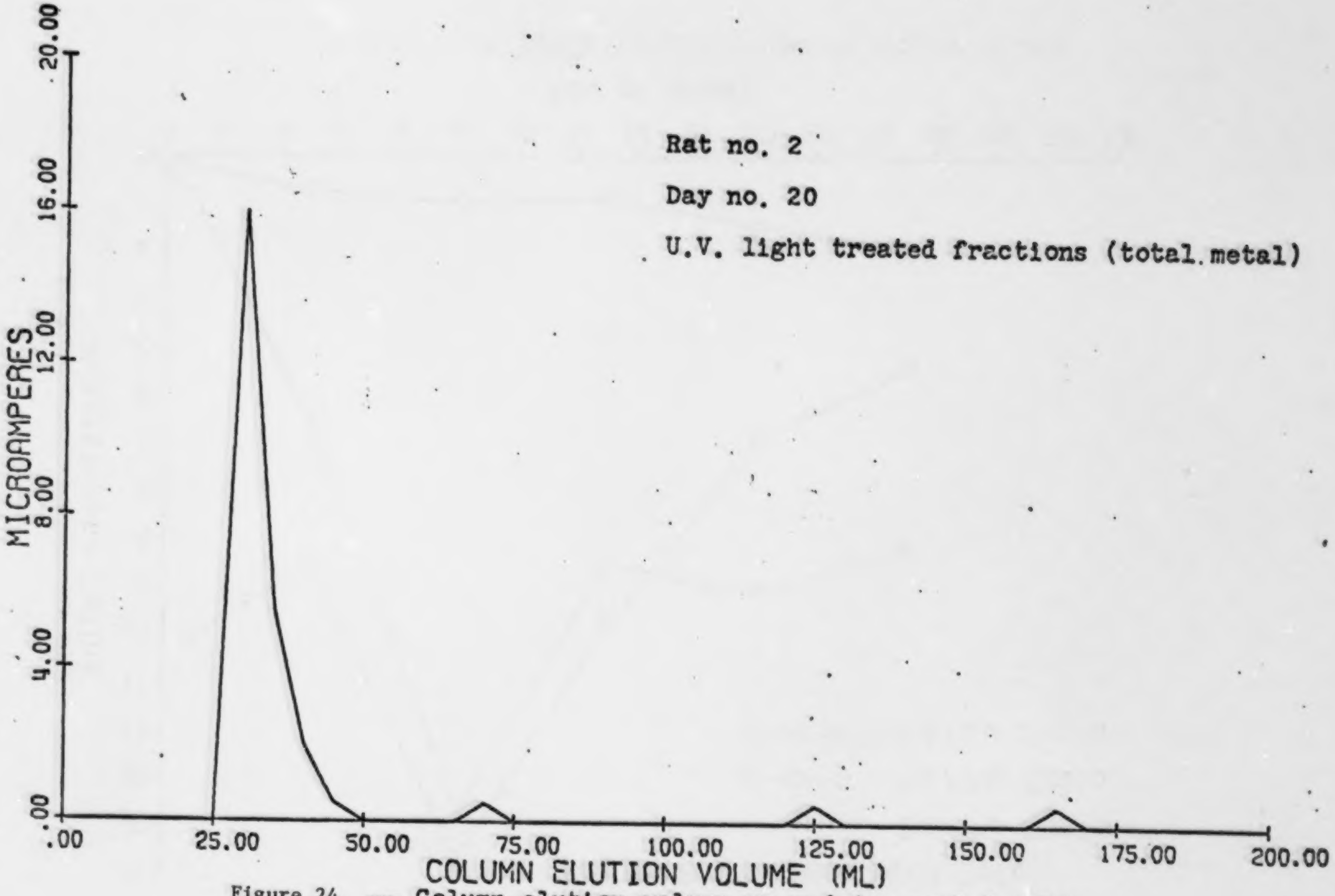


Figure 23. -- Column elution volume vs cadmium peak height



Rat no. 2

Day no. 20

U.V. light treated fractions (total.metal)

Figure 24. -- Column elution volume vs cadmium peak height

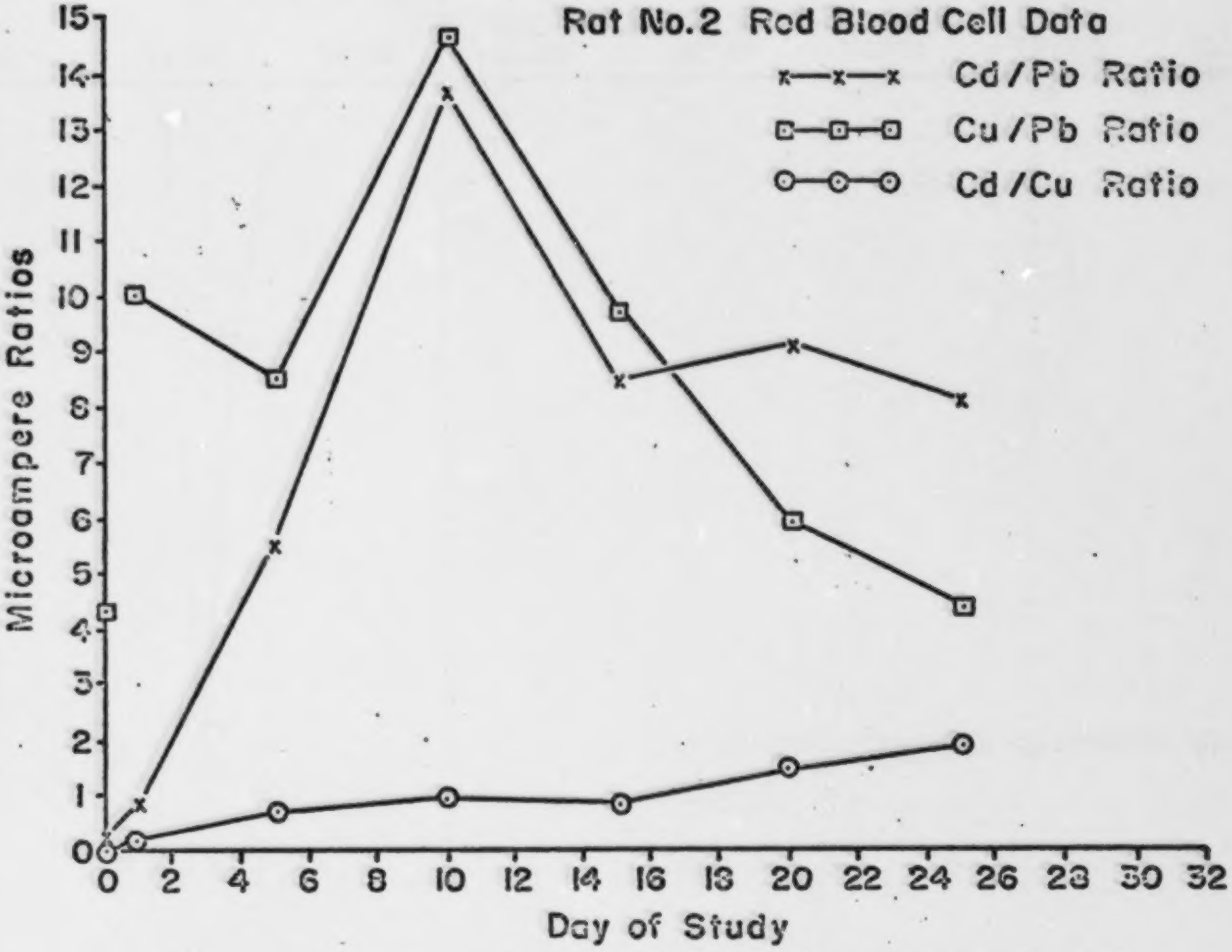


Figure 25. -- Peak height ratios vs day of study

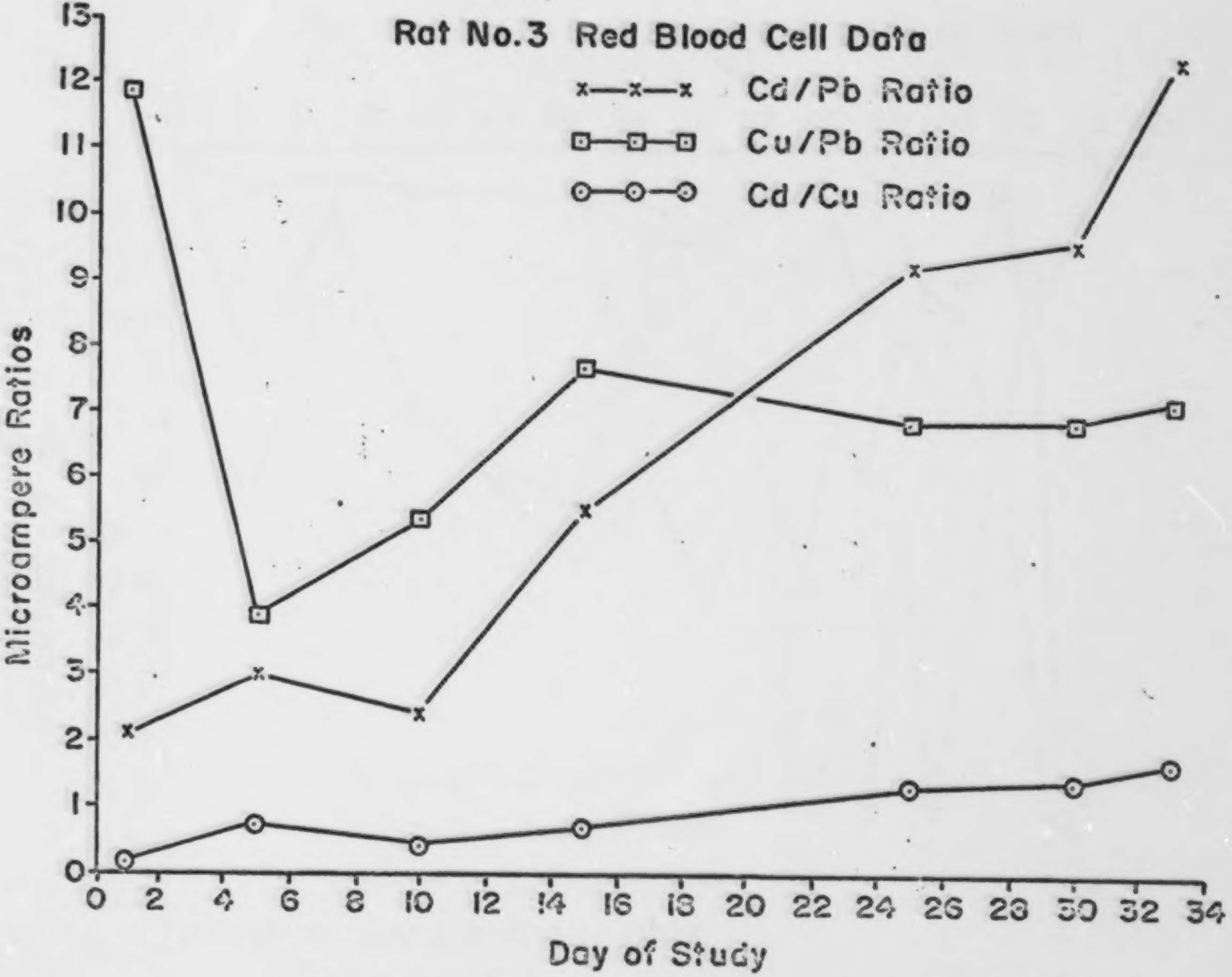


Figure 26 - Peak height ratios vs day of study

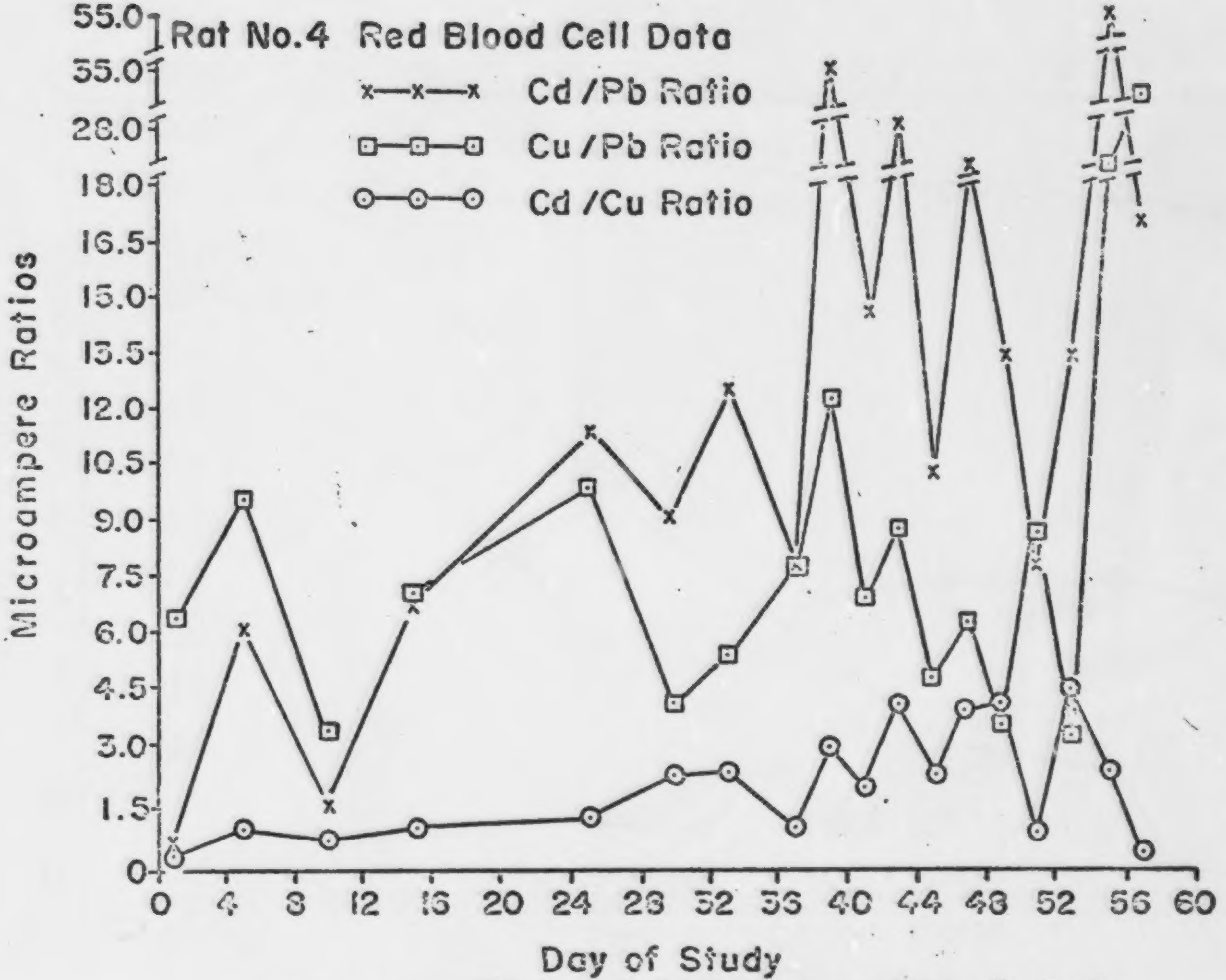


Figure 27 -- Peak height ratios vs day of study

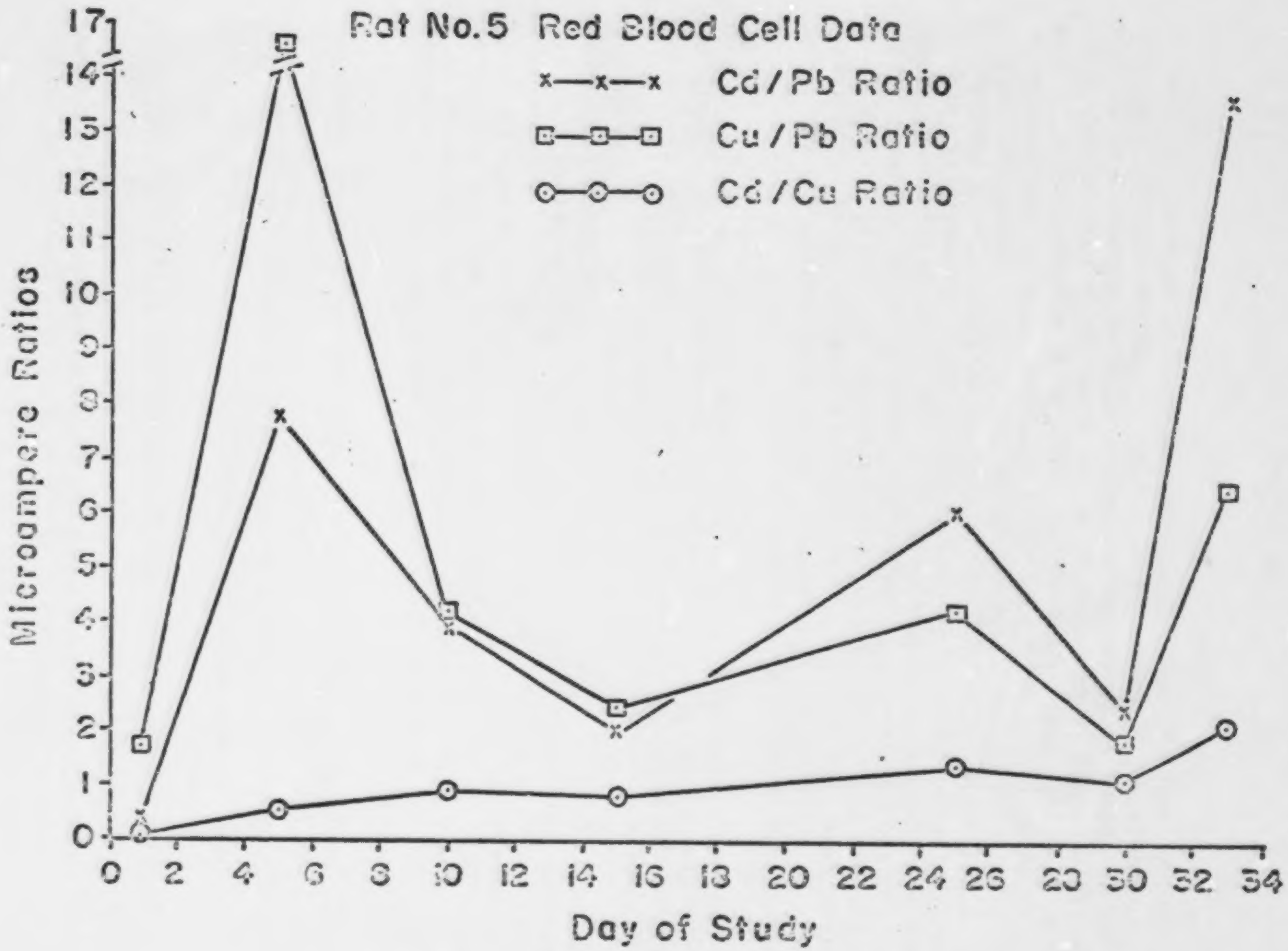


Figure 28 -- Peak height ratios vs day of study

THE ION MICROPROBE *

M. Bayard

For the past 13 years the electron microprobe has been the best tool available for elementary analysis of ultramicro samples. Using a crystal spectrometer or energy dispersive solid-state device to analyze x-ray fluorescence generated in $2\ \mu m^3$ of sample by a beam of electrons 1 μm in diameter, the instrument has, on a solid solution basis, a sensitivity which ranges from 5000 to 50 ppm, depending on the element of interest and the matrix in which it is dispersed; a detection limit which ranges from about 10^{-14} to 10^{-16} g of material; and a routine accuracy of ±5%. At present, the detection limit, sensitivity, and accuracy of the electron microprobe have almost reached the theoretical limit imposed by the white x-radiation generated in the electron excitation process and by the fairly large volume of the sample excited by the electron beam. In addition, the electron microprobe is severely restricted in the analysis of elements lighter than sodium. In fact, the first three elements cannot be seen at all.

The newly-developed ion microprobe mass analyzer (IMMA) extends the capabilities of the electron microprobe, overcomes most of its shortcomings, and, in addition, allows some analyses not heretofore possible of micro samples. The x and y resolution of IMMA is similar to that of the electron probe, but the z axis or depth resolution is generally at least 1000 times better. Because there is no mechanism for white radiation generation, the instrument is capable of sensitivities around 0.01 ppm or better and detection limits approaching 10^{-19} g when instrument noise and cross-talk between adjacent ion peaks are reduced as much as is practical. IMMA detects all elements from hydrogen up and performs quantitative analyses with a routine accuracy of ±3%. Table 1 provides an example of IMMA detection limits. The following list gives the noteworthy features of IMMA.

1. Isotopes of all elements are digitally measured and displayed on the video readout system.
2. Analysis is achieved in depth with monolayer sensitivity.
3. The ion beam diameter is continuously variable from 2 to 300 μm.
4. It employs a mass-analyzed monoisotopic primary ion beam.
5. Sensitivities range from ppb to ppm.
6. Isotope abundance ratios are directly measured; presentation is both digital and on video readout as a function of beam position on the sample.

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* Published in American Laboratory, April, 1971.

Design and construction of IMMA

IMMA is somewhat analogous in operation to the electron microprobe: A spot of ions about 1 μm in diameter is formed on the sample surface with an ion source focused by two electrostatic lenses. The primary ions, either a reactive gas such as F^- or a very heavy inert gas such as Ar^+, react with the sample and sputter off secondary ions. These secondary ions are collected by a high angular aperture mass spectrometer and analyzed to determine both the elements and isotopes present in the sample volume, typically 1-5 μm in diameter by only a few monolayers thick. Figure 1 shows the organization of the various components of IMMA.

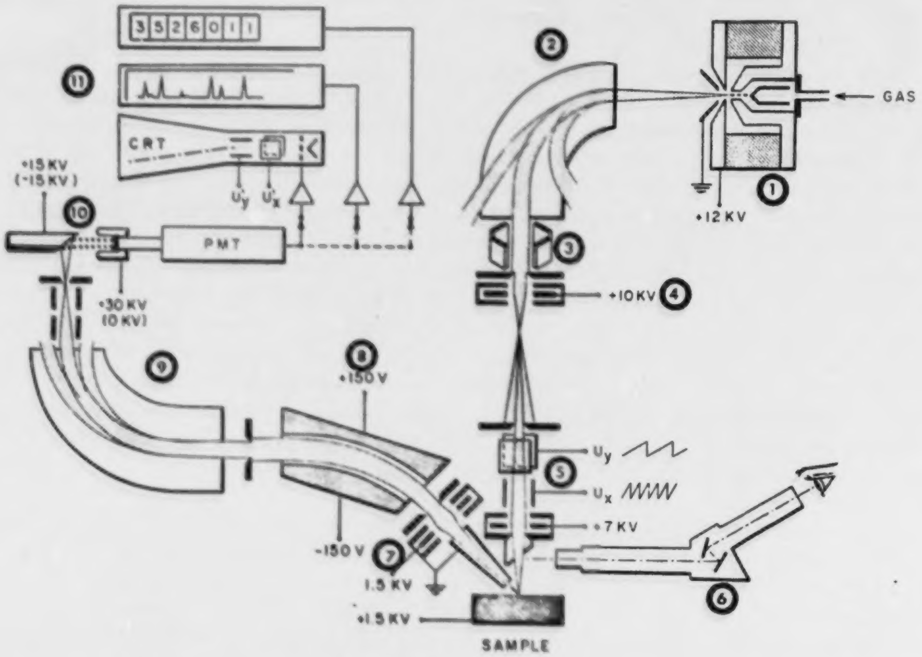


Figure 1. Schematic cross section of ion microprobe mass analyzer.

(1) Duoplasmatron ion source. (2) Primary mass filter which allows only one species of ion into optical column. (3) Alignment deflector plates. (4) First electrostatic condenser lens. (5) Second electrostatic condenser lens and beam-scanning deflector plates. (6) Optical microscope to view sample during analysis. (7) Lens to extract ions from sample. (8) Electrostatic velocity sector of analytical mass spectrometer. (9) Magnetic mass analyzer of spectrometer. (10) Ion detector and photomultiplier tube. (11) Readout electronics--oscilloscope, strip-chart recorder, and scaler.

The source of ions is a duoplasmatron, a device using axially symmetric electrostatic and magnetic fields to move electrons and the gas which is being ionized in fairly long spiral paths through the device. Because of the long path length, the chance of an ionizing collision is high, and practically any gas, even air, can be used to give a high brightness source of either positive or negative ions; shifting rapidly from nitrogen to oxygen ions is also possible. The duoplasmatron will produce doubly ionized species and, in some cases, ionized molecular fragments. Since it is desirable to have only one type of ion interacting with the sample, a 90° bend electromagnet is used as a primary mass filter at the entrance to the electrostatic lens column. The magnetic field is adjusted so that only the desired type of ion is deflected into the lenses, and other types are deflected more or less, depending on their mass-to-charge ratio.

As mentioned previously, two electrostatic lenses successively demagnify the source and focus the ion beam. It is unfortunate that the electrostatic lenses must be used since magnetic lenses of equivalent demagnifying power have a much lower spherical aberration, the factor which limits the formation of ion spots less than 1 μm in diameter with ion currents high enough to be useful. Since, however, conventional axially symmetric electromagnetic lenses are weak focusing devices, utilizing only second-order focusing by fringe fields, they cannot handle the mass of the ions in the beam, and electrostatic lenses must be used instead. Even an H+ ion, that is, a proton, weighs 1836 times as much as an electron, so that it is no wonder that the magnetic lenses used in the electron microprobe do not work, for example, on Ar+ ions. In the future, there is the possibility of using strong, focusing, asymmetric magnetic lenses such as quadrupoles or octopoles and achieving spot sizes of less than 0.1 μm with useful currents.

In addition to the electrostatic lenses, the ion optical column has a beam-scanning system that consists of electrostatic deflection-plate sets which allow the beam to move an x-y faster on the sample in synchronism with the spot on a cathode-ray tube. The net result is an ability to build an image of the sample surface, showing the location of any chosen ion species. The resolution, on the order of 1 μm, is the same as the spot size.

The mass spectrometer performs two functions. First, its electrostatic sector sorts the ions on the basis of velocity and brings most of them to a similar speed. Next, its magnetic sector sorts the ions on the basis of mass-to-charge ratio. Only those ions having a discrete, selected m/q are passed through the exit slit to the detector. It is a simple matter to vary the magnetic field strength and thereby scan the entire mass range from 1 to 300 in less than 30 sec. An electrostatic lens increases the angular aperture of the system. Between 4 and 10% of the ions escaping the sample are collected by the spectrometer.

A second type of mass spectrometer, available for use with IMMA, contains an electrostatic immersion lens to extract and image the ions. The spectrometer itself consists of two 90° magnets with an electron mirror for velocity correction. The device, capable of point analysis and scanning, becomes a nonscanning ion microscope with about a 1-μm resolution.

Capabilities and applications of the ion microprobe mass analyzer

The interactions of the sample and the primary ion beam are complex, depending partly on the type of ion in the primary beam and its accelerating potential. Generally, when the ion beam first strikes an area of the sample, the secondary ion yield is erratic until a reactive layer forms on the sample and a steady state is reached. The ion yield is then relatively constant, and quantitative analysis can be attempted. Since the reactive surface chemistry depends somewhat on the chemistry of the sample, some information about the compounds in the sample can be inferred from the time required to reach steady yield. However, because of the initially erratic yield, quantitative analysis of the first few monolayers of a sample can be difficult. In the cases where the sample is larger than the beam diameter, a steady state can be achieved and the beam slowly moved to the area of interest while maintaining steady ion yield.

Quantitative analysis with IMMA is relatively easy. It does require fairly complex computer reduction of the data, but the reliability of these data is better than that of the computer-reduced results from the electron microprobe, where oxygen is frequently done by difference as 40 or 40.00%. Because IMMA does not suffer as much as the electron probe from surface geometry and depth inhomogeneities, the accuracy one can expect from the instrument is about ±3% routinely and ± 1% in some cases.

The destructiveness of the method is still a matter of debate. At least 100, preferably several thousand, atomic layers should be analyzed to give reliable information about a sample, and by the most rigid definition, some surface layers of the sample are lost. However, if the sample is a gross metallurgical or petrographic section, the amount of sample degradation will be very small. In some instances, moreover, the destructive nature of the technique can be put to very good use; in such multiple layer samples as solid-state electronic devices, the top layer may be analyzed and sputtered away to allow analysis of succeeding layers. The rate of sputtering may be quite high, 1-5 μm/min., so fairly deep holes can be bored in the sample, and an "in depth" analysis performed. Alternatively, the rate can be reduced and a few monolayers sputtered off at a time for analysis. This procedure is very difficult to perform by any other technique and directly contrasts with the maximum and minimum analytical penetration capabilities of the electron probe. The maximum for the electron probe is on the order of 5-10 μm and the minimum is generally a few tenths of a micrometer.

IMMA has many varied applications. Practically any problem solvable by electron probe analysis can be solved by IMMA, most likely with a considerable savings in time. As illustrated by three specific examples:

The analysis of defects and contamination on integrated circuit (I.C.) devices is usually a very simple matter with this instrument; the ion probe solved each problem after electron probe analysis was partly or totally unsuccessful. In the first case, two gold-coated ceramic bases for I.C. contacts were examined by electron probe and shown to be essentially identical. However, one sample bonded to the I.C. chips perfectly, the other not at all. IMMA showed nickel, silicon, carbon, and a trace of tungsten in the contact areas of the bad sample; the nickel was present as about 2 ppm in a surface layer only 100Å thick. Small amounts of carbon and tungsten were found in the good sample. The trouble was eventually traced to faulty operation of the vacuum-coating unit which formed the gold contacts. In this problem, the electron probe would have required at least 600 times more nickel for detection.

A second example of an integrated circuit problem solved by IMMA involves a case where the electron probe could provide some, but not enough, information to really satisfy one's curiosity about the problem. In this case, a layer of tin, tin oxide, or tin hydroxide was forming on the aluminum metallization of the I.C. and pulling the metal away from the devices it was supposed to connect. IMMA, able to dissect various layers, indicated a surface layer about 40% tin oxide and 60% hydroxide and a lower layer in contact with the aluminum that was tin with a trace of tin and zinc chloride. Apparently a poor soldering operation allowed some flux and metal to migrate and plate on the surface. The change from metal to oxide caused a dimensional change which pulled the aluminum from the substrate.

In the last example of an I.C. problem solved by IMMA, a phosphated glass layer was coating the circuit. Maximum phosphate in the layer immediately under the glass should have been 0.05 ppm in a layer only 2000 Å thick, but the actual amount was in question. The electron probe was unable to make this determination because it had no way of seeing the low phosphate layer under the glass. The ion probe indicated 0.04 ppm phosphorus ±0.01 ppm --after the glass had been sputtered away with the ion beam.

Diffusion profiles are a perfect subject for IMMA. For example, a 0.7-μm thick area of a gold-palladium-nickel contact was examined to investigate the diffusion of gold. Three distinct layers, with 60% gold and 40% palladium on the surface, were easily seen. Again, the ability of IMMA to remove thin layers and analyze them has been proved the easy solution to the problem. Polishing away 0.1-μm increments and then electron-probing at low accelerating voltage had been tried, but problems with smearing while polishing and the limited sensitivity of the probe rendered the results of this method very dubious.

The organic analytical ability of IMMA has yet to be fully explored. However, samples should be analyzable in the ion probe, although with considerable difficulty. The general scheme is to fragment the organic material into charged molecules for analysis, a procedure that does not differ from conventional organic mass spectroscopy except insofar as the ionization process tends to form small fragments. The ratios of the various light elements in organic material can be done quite easily. There is a possibility of using heavy organic radicals, such as triphenylmethyl in combination with fragments of the organic material in question.

A similar mode of analysis can be attempted on inorganic compounds. Several types of available information at least indicate the compound that may be present: the rate of steady-state formation, the ratio of elements when the exciting ion species is changed, and the formation of charged molecular fragments. However, as with the electron microprobe, the main information available is elemental, not chemical, composition.

In the analysis of small particles, IMMA has advantages over most other techniques. The electron microprobe can determine the major components, i.e., those above 5% by volume, of particles as small as 1000 Å and generally can see only elements heavier than $Z = 11$. IMMA allows sensitivities on the order of 0.1% of particles 1000 Å in diameter, and the light elements offer no special problem. The main problem is handling and mounting small particles; at present the best way seems to be pressing the particles into a block of pure indium.

Finally, there is one type of analysis not possible with any other instrument: the isotopic analysis of microsamples. On a sample of a pure element, isotopic abundances on the order of 1 part in 10^7 are visible. Paleoclimates of marine fossils can be determined because of the difference in the solubility of oxygen 16 and oxygen 18, bound as either silicon dioxide or calcium carbonate in the shells of marine organisms such as diatoms or foraminifera; this type of information can be derived from a single microfossil only 50 μm across. Dating rock material by radiogenic lead determination is possible in samples with a relatively high concentration of radiogenic lead. Potassium-argon ratios can also be used on relatively small samples. The samples to be analyzed for isotope dating will be fairly large, on the order of 300-500 μm in diameter, in order to achieve adequate counting statistics.

In summary, the ion microprobe mass analyzer is presently the best tool available for ultra-micro analysis. Its ability to do trace analysis on small particles, their films, and other ultra-micro specimens has long been desired. Its detection limit approaches that required for all practical applications. One hundred thousand atom quantities of material can be routinely handled with this instrument.

THE CLINICAL CHEMIST'S RESPONSIBILITY IN ENVIRONMENTAL HEALTH

G. N. Bowers, M.D.

Introduction

Many persons are not familiar with clinical chemistry or the professional chemist who is responsible for a hospital chemistry laboratory --the clinical chemist. Perhaps one can best define a clinical chemist as the analytical chemist of the hospital or of the medical arena who must translate a doctor's written orders for a chemical test on body fluids or tissues into a meaningful quantitative measurement. The concern is for accurate measurement, encompassing every aspect of the entire medical measurement system (i.e., sampling, transporting, measurement, and interpretations) as suggested in Figure 1.

It is only natural that the chemical agent(s) in the environment which result in significant biochemical distortions and disease are of just as much interest to the chemical analyst as to the physician, the public health worker, or the environmental scientist. Together with his clinical peers, the laboratory scientist cannot ignore the *biological reality* that certain chemical agents are injurious to living cells, no matter how valuable to our technology and economy. Thus, the health laboratory scientist--be he clinical chemist, hematologist, bacteriologist or pathologist--has a real contribution to make in the area of environmental health. In this paper I would like to review with you some of my experience as a clinical chemist and a physician interested in the interactions between the element lead (Pb) and our environment. One could just as well have chosen asbestos, beryllium, cadmium, chromium, detergents, herbicides, mercury, or pesticides, etc., to illustrate this vital relationship.

Acute Lead Poisoning

Man has poisoned himself or his fellow man with lead since 2500 B.C. when the first smelting of lead ore caused toxic exposure to lead fumes. Industrial exposure to lead fumes or dusts has been progressively controlled by legislation, industrial hygiene, and workmen's compensation programs. As pointed out in a wonderful review article entitled *Lead Poisoning*, by Chisolm *(1)* of John Hopkins:

> "The more immediate and urgent problem is to control the exposure to lead of well-defined groups that are known to be directly at risk: young children who live in dilapidated housing where they nibble chips of leaded paint, whiskey drinkers who consume quantities of lead-

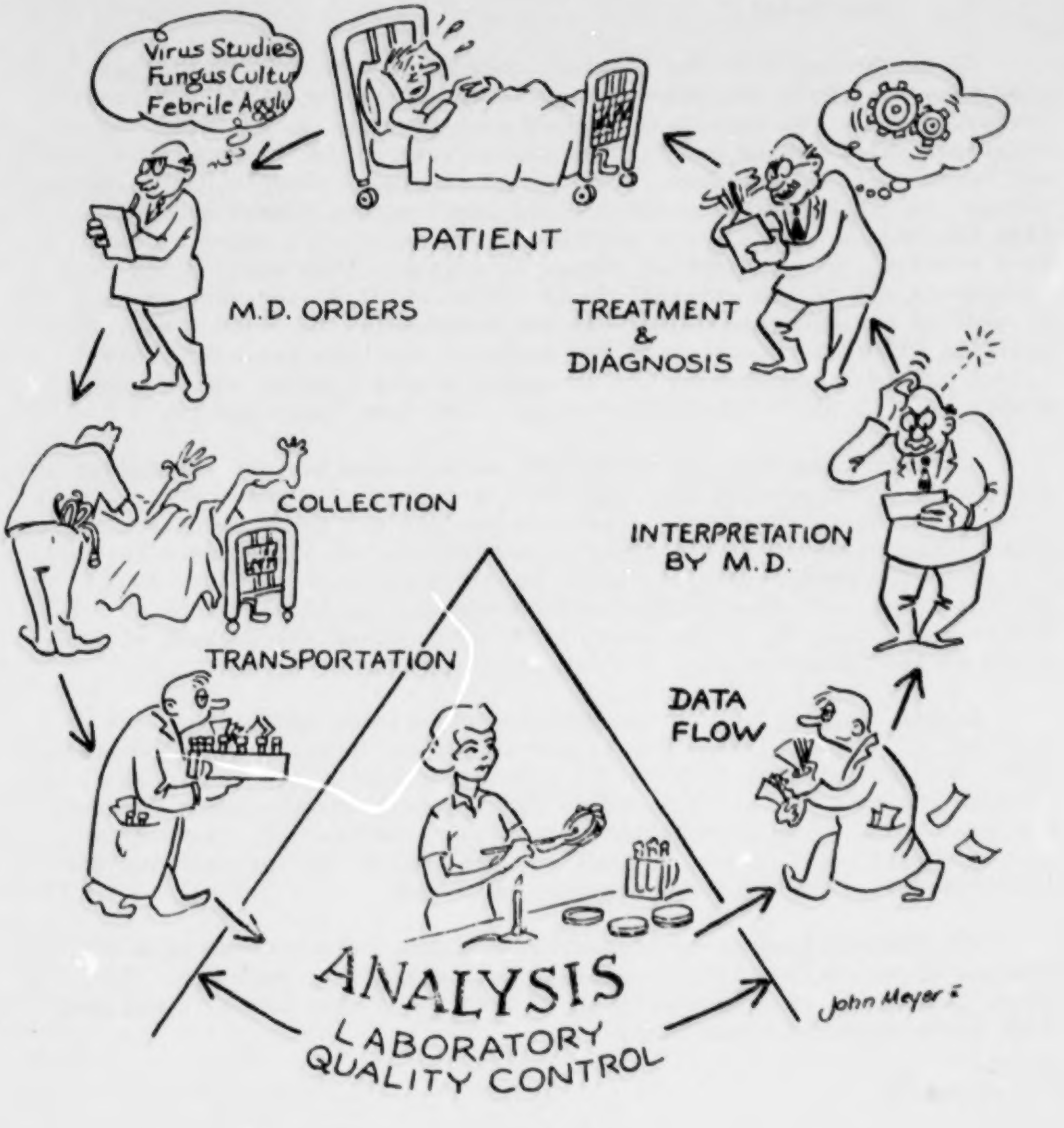

Virus Studies
Fungus Cultu
Febrile Agglu
PATIENT
M.D. ORDERS
TREATMENT & DIAGNOSIS
COLLECTION
INTERPRETATION BY M.D.
TRANSPORTATION
DATA FLOW
ANALYSIS
LABORATORY QUALITY CONTROL
John Meyer

Fig. 1. Laboratory quality control represents only a small segment of the ultimate objective of the clinical chemist: Improved medical care through better application of laboratory observations.

contaminated moonshine; people who eat or drink from improperly lead-glazed earthenware, workers in certain small-scale industries where exposure to lead is not controlled."

It is obvious that the clinical chemist must provide blood lead analysis to support the diagnosis and treatment of acute lead poisoning. However, only a few hospitals provide such services as emergency determinations which can be used in the rapid differential diagnosis of coma and convulsions in children. The "environmentally responsible" clinical chemist must, therefore, provide blood leads within a more meaningful time period and assure their accuracy! Unfortunately, existing data from surveys *(2)*, as shown in Figure 2, suggests that whole blood lead determinations at the critical 50 to 100 µg Pb/dl WB may vary as much as ±50% of the measured value. In our laboratory, Mr. John Pybus, a visiting clinical chemist from New Zealand, has been perfecting his former red cell lead method *(3)* to assure a more precise and accurate assay, using 5 ml of heparinized whole blood (see Appendage A).

Although flameless AAS micro-lead methods are heavily advertised at present by the companies offering AAS instruments for sale, we presently know of no one in a service laboratory who has had great success with these interesting devices. There is, therefore, an urgent need for substantially more work by clinical and/or analytical chemists to perfect blood lead measurements and demonstrate by objective-blind survey data that this toxic element can be measured in clinical situations at the 5% rather than the 50% accuracy level!

I shall not attempt to describe our experience with acute lead toxicity in small children due to the ingestion of paint, for it parallels that described by Chisolm *(1)* and many others. However, a study of several hundreds of children from a rural area in northwestern Connecticut vs. a poor urban area in the north end of Hartford is showing two very distinct populations, suggesting that another factor--perhaps air lead--is more important than formerly believed.

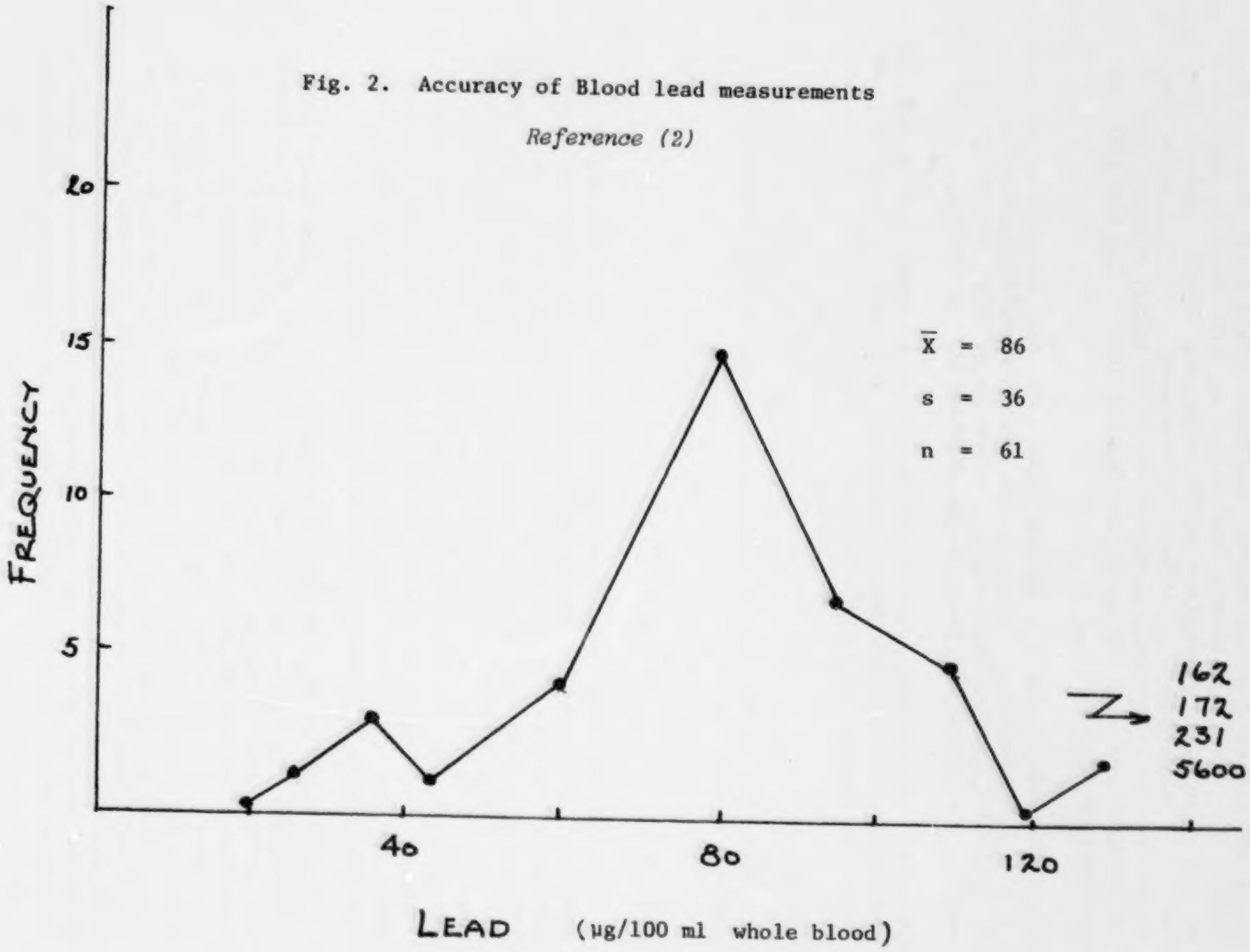
The following two case histories, however, document the need for constantly suspecting lead toxicity in all diagnostic problems. If blood leads were readily available in local hospitals and clinics, many such cases would be discovered!

Case #1

A 34-year-old married female supervisor had poorly-defined complaints of fatigue, weakness and excessive drowsiness in the early evenings. She volunteered as a "control" for blood lead measurements as a part of a research study, and repeated determinations were twice as high as other controls. Her levels ran between 30-40 µg Pb/dl WB over a year's period of observation. An intensive search for a source of excessive lead exposure uncovered an Italian hand-crafted coffee mug which she had been

Fig. 2. Accuracy of Blood lead measurements

Reference (2)



using daily which leached enough lead into coffee to give 1-2 mg Pb intake/day. This coffee mug leached 230 mg Pb/l after 12 hours in 4% acetic acid, in comparison to 100 other mugs which revealed only one other above 2 mg Pb/l after a 12-hour soak. Further investigations showed urinary lead to be <50 μg Pb/24 hours; however, urinary coproporphyrins were 200 μg/24 hrs (normal <161). The hemogram was entirely normal.

After eliminating the 1-2 mg lead intake per day, blood lead was reduced considerably. Within months all symptoms disappeared. No chelation therapy was initiated since 50 μg Pb/dl WB was usually considered the point at which treatment is given.

Comment: Occult lead toxicity may be far more common than we believe. When accurate blood lead measurements are available it is almost certain that limits which are consistently associated with symptoms may drop to 25 or 30 μg Pb/l WB. Accurate measurement is essential to further progress in this area. One should read the recent case report of a death in Canada reported in the *New England Journal of Medicine (4)* to more fully appreciate how widespread toxicity from lead-glazes can be.

Case #2

A 34-year-old woodsman was hospitalized with a history of abdominal pains and a numbness and weakness of the hands and feet. Laboratory examination revealed an anemia, and in the course of the investigations a urine lead was found to be 1020 μg Pb/24 hrs (normal <150). After treatment with calcium EDTA, the urine leads rose over 4000 μg Pb/24 hrs after each of two treatments. The patient was diagnosed as having lead poisoning with a severe peripheral neuropathy. Review of work habits revealed that this man used a powered chain saw for many hours each day, often for weeks at a time. This saw was driven by a small engine using leaded gasoline *(5)*.

Comment: Exposure to exhaust fumes has frequently been associated with higher blood lead levels, but this case illustrates how extreme and intense such exposure can be. The failure to obtain blood lead determinations and reliance on urinary lead is a mistake (except in very acute disease) since, as shown in Case #1, urine is a poor indicator of chronic exposure. Blood leads, not urine lead, should be utilized in all diagnostic problems except to see how much lead is mobilized after EDTA diagnostic challenge or in treatment. Major dependency should be on blood leads; this woodsman's levels were probably between 100-120 μg Pb/dl WB before treatment--certainly follow-up should be with repeated blood leads at monthly intervals.

Atmospheric Lead

I was first introduced to the subject of environmental lead pollution on reading an article entitled, *Contaminated and Natural Lead Environments of Man*, in 1965 *(6)*. The author was a distinguished geochemist, Dr. Claire Patterson, who had dated the age of the earth thrugh isotopic lead measurements. This dating was made by quantitating the minute proportions of stable lead isotopes resulting from the radioactive decay of thorium and uranium by mass spectroscopy. The overwhelming analytical problem was contamination of these minute amounts of isotopic lead by the traces of lead found in distilled water, glassware, reagents, and even carefully-filtered laboratory air. As one might expect, success in dating required elaborate precautions to exclude this contamination from environmental lead. Given these technical problems, it is not surprising that Dr. Patterson was aware of the pervasive nature and of the degree to which lead was present in our environment. Fortunately, Dr. Patterson was not silent about what disturbed him and his response was to organize "what was known about the occurrence and distribution of lead in natural and contaminated environments into a coherent study, and publish it." *(7)*

Natural vs. normal blood and total body lead

From the relationship of alkaline earth group metals found in soils, plants, and animals, Patterson postulated an enhancement-exclusion principle to explain the abundance of the lighter metals and the absence of heavier metals in plants and animals. He calculated as a result of this principle that natural man (before 2500 B.C., when lead usage first began) probably had whole blood lead levels of less than 10 micrograms per liter and total body lead burden of less than 10 mg per 70 Kg. Contrasting today's average adult levels of whole blood of 200 μg/liter and total body lead burden of 200 mg/70 Kg, he strongly suggested that the United States population bore a chronic lead insult which was probably associated with unrecognized adverse effects. This publication creased a furor, especially in the ranks of the industrial and occupational health professionals, as well as in some public health officials. Some questioned the propriety of a geochemist making implications about medical, toxicologic, and public health aspects of human lead exposure.

Interestingly enough, although little of the data had as yet been published in 1965, other investigators were also uneasy about the increasing lead observed in urban versus rural airs, in rain waters, in snows, and in the oceans, as well as in soils, plants, shrubs, trees, and animal life exposed to vehicular exhaust. For example, Cannon and Bowles *(8)* had reported lead accumulations in soils and in grasses adjacent to highways (Figure 3). In 1968, Schroeder and Tipton combined their years of separate research efforts in a publication which gave data on total body lead *(9)*. They showed that Americans with each passing year were accumulating more lead in their tissues than Europeans, Asians, Africans (Figure 4). Since persons known to have had any occupational exposure to

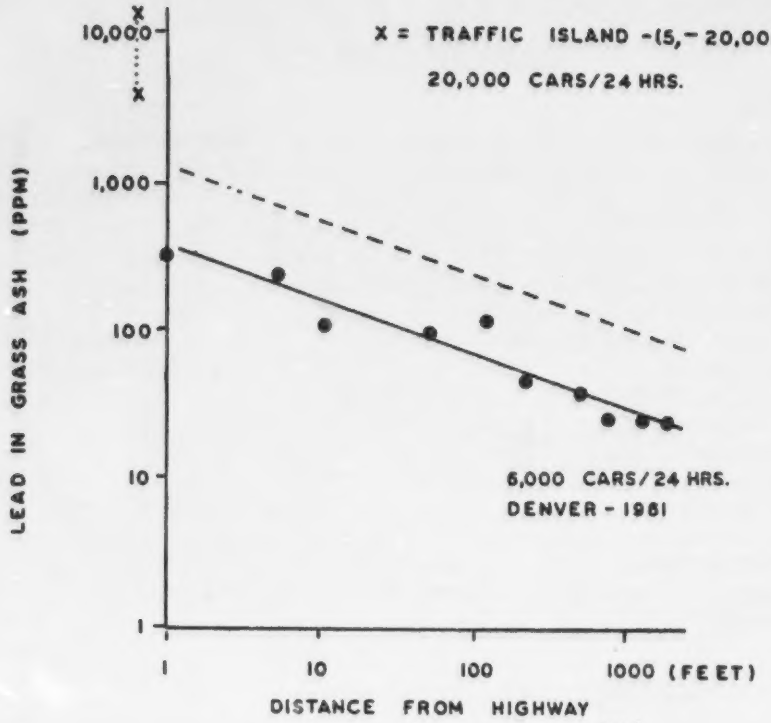
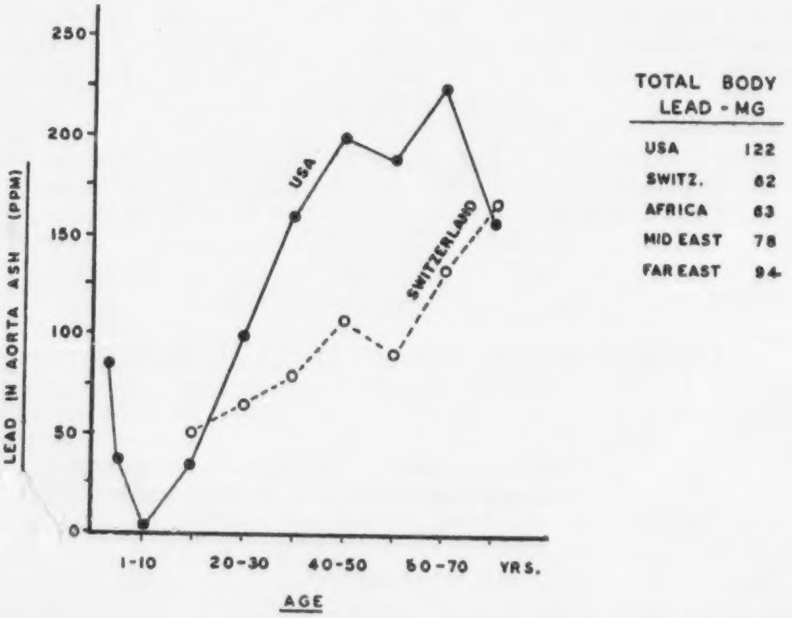


Fig. 3. Lead accumulations in soils and grasses adjacent to highways.
Ref. (8)



TOTAL BODY LEAD - MG	
USA	122
SWITZ.	82
AFRICA	83
MID EAST	78
FAR EAST	94

Fig. 4. Tissue lead levels in people of different geographic locations.
Ref. (9) *Ref. (9)*

lead were excluded from these studies, lead came from food, water, or air. Table 1 shows sources of lead ingestion or inhalation, the fractions absorbed, and the amount absorbed per day by American adults.

Table 1.–Injestion and Absorption of Lead by Contemporary Man*

Substances	Intake/day	Lead Concentration	Lead Injested or Inhaled	Fraction Absorbed	Lead Absorbed
Food	2 Kg	0.2 mg/Kg	400	0.05	20
Water	1 Kg	0.01 mg/Kg	10	0.1	1
Urban air	20 m^3	1.3 $\mu g/m^3$	26	0.4	10
Rural air	20 m^3	0.05 $\mu g/m^3$	1	0.4	0.4
Tobacco smoke	30 cigarettes	0.8 μg/cigarette	24	0.4	10

* Source: C. C. Patterson, see reference number 6, Table number 7.

Most observers agree that lead in food and water is generally decreasing; but lead in air--especially urban air--is steadily increasing at 5-10% per year. Since 40-50% of lead in air is small enough to reach the alveolar spaces where nearly total absorption occurs, there is reason to be concerned with rising levels of atmospheric lead. Thus, in agreement with Patterson, the geochemist, Schroeder, a physician long respected for his excellent trace metals research, warns: "It is likely that atmospheric lead from motor vehicle exhausts largely account for increased exposure and that inspired lead may make up a sizeable proportion of the total amount absorbed by the body. In view of the steadily increasing annual pollution of air and soils with lead from motor vehicle exhausts, innate toxicity in exposed human beings may appear." *(9)* Recently public health officials have become more concerned about atmospheric leads potential health effects, and Hunt *et al.*, *(10)*, after studying cadmium, zinc and lead in 77 Midwestern cities in 1968, stated: "preliminary analysis has shown a positive relationship between lead dustfall in residential areas of the 77 cities and cardiovascular mortality."

Atmospheric lead from gasolines *

In December 1967, roughly two years after Patterson's paper forced the U. S. Public Health Service to hold a special White House Conference *(12)* on the subject of environmental lead contamination, the Swedish Royal Commission on Natural Resources received a detailed report entitled *"Gasolines Containing Lead"* from its staff member L. Danielsson *(13)*. Danielsson's report covered the early history of introduction of tetraethyl lead additives to gasoline, the evidence of widespread environmental pollution from lead, especially in the United States, and documents why each passing year brings increases in the amount of lead reaching the atmosphere from motor vehicular exhaust. In Sweden, as elsewhere, the main contributing factors were:

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* Portions of this section taken from a prior publication *(11)*.

(1) A 7% yearly rise in the number of motor vehicles, especially in the cities.

(2) A 6% yearly increase in mileage driven by each car.

(3) And a 6% increase of lead due to higher octane gasolines (from 0.49 gm/liter in 1963 to 0.84 gm/liter in 1967).

Similar trends were also at work in our own country. In 1958-59 the U.S. Public Health Service permitted the maximum allowable tetraethyl content of gasoline to go from 3 ml to 4 ml per gallon *(14)*. Today all urban areas in the U.S. are experiencing rises in atmospheric lead, particularly along heavily-travelled streets and highways. Bove and Siebeherd *(15)* measured the relationship between lead, carbon monoxide, and traffic density on New York City's 45th Street, as shown in Figure 5.

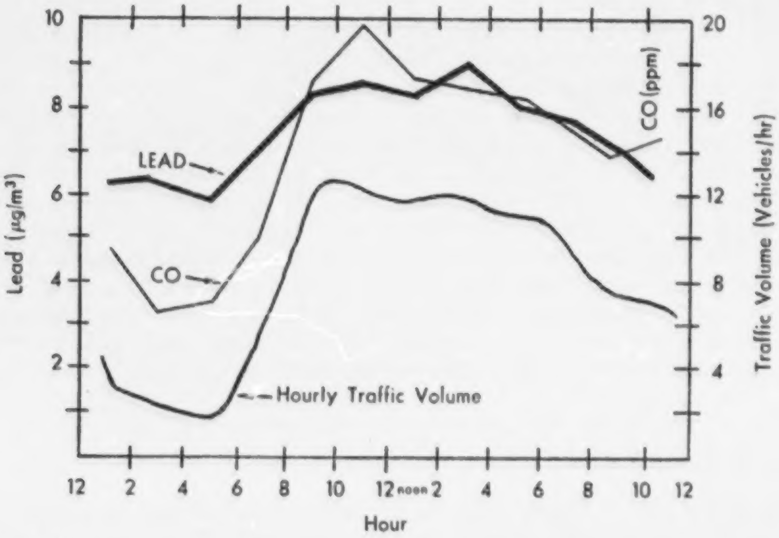

Fig. 5. Relationship between lead, carbon monoxide, and traffic density on 45th Street (New York City). *Bove et al., (15)*.

Since there is a direct relationship between atmospheric lead and whole blood lead levels, as shown in Table 2, urban dwellers rapidly accumulate more lead than their rural neighbors.

Table 2.-Relationship Between Lead in Atmosphere and Lead in Blood*

Type of population	Estimated exposure (micrograms/cu. meter)	Mean blood lead (microgram/100 g.)
No occupational exposure:		
Remote California mountain resident	0.12	12
Composite rural U.S.	0.50	16
Suburban Philadelphia	1.0	13
Composite urban U.S.	1.0	21
Downtown Philadelphia	2.4	24
*L.A. resident living near the coast	0.34	16
*L.A. resident living near a freeway	2.5	22.7
Occupational exposure:		
Cincinnati policemen (all)	2.1	25
Cincinnati traffic policemen	3.8	30
Cincinnati garage workers	5.5	31

* Source: D. Forman from Scientist's Committee for Public Information Inc. March 13 1969 (New York Chapter).

Chou *(16)* has recently shown by mass spectroscopy that the isotopic leads in urban air and leaded gasoline are similar, thus providing evidence that the overwhelming source of lead polluting the atmosphere was from gasolines. His studies showed that Mid-Pacific marine air contained only 0.001 µg Pb/m^3, while 1000 feet offshore at LaJolla, California, air measured 0.4 µg Pb/m^3. Likewise, on remote 6100-foot-high Laguna Mountain, 45 miles east of San Diego, air samples average only 0.05 µg Pb/m^3, while air sampled in downtown San Diego gave a yearly mean in excess of 2 g Pb/m with seasonal variations from 1 µg Pb/m^3 to 4 µg Pb/m^3 and occasionally peaks of 8 µg Pb/m^3 during thermal inversions.

Danielsson's report went to some lengths to show that the concepts about the potential hazards from atmospheric lead which prevailed in the U. S. Public Health Services prior to Patterson's paper in the fall of 1965 were strongly influenced by Kehoe.* Kehoe maintained, on the basis of his voluminous published studies, including several balance studies on humans ingesting *(17)* and inhaling *(18)* lead, that increased exposure to and absorption of lead was compensated by increased excretion, with no harmful effects and little or no build-up of lead in tissues. Kehoe further maintained that deposits of body lead were in a state of reversible equilibrium with the environment *(19)*. Danielsson's critical re-examination of these balance studies suggested that lead was not eliminated completely, even over long periods of time, but was accumulating at rates which might well have given classical signs and symptoms of lead toxicity had the experiments been continued longer. From study of all available literature around the world, including Russian data, he advanced the thesis that the maximum daily permissible dose of lead absorbed from all sources should not exceed 10 μg Pb/day. Since required daily intake of food and water now contributes this amount, he suggested that *no* lead can be permitted in the atmosphere if occult chronic damage from lead is to be avoided. His report, therefore, calls for the removal of all gasoline in Sweden.

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* Both Patterson and Danielsson remark that the Kettering Institute was heavily financed by funds from the Ethyl Corporation and that Kehoe himself was for years the chief medical-toxicologic consultant to the Ethyl Corporation.

Distant effects of lead aerosols

Motto, *et al.*, *(20)* in a paper *Lead in Soils and Plants: Its Relationship to Traffic Volume and Proximity to Highways,* suggested that the major effects seem to be related to heavy lead particles which drop to the earth within several hundred feet of the road. In 1967, Page and Ganje *(21)* deliberately resampled soils one mile or more from California highways and compared them with soils collected between 1919 and 1933 at the same locations and depths. In general, as shown in Table 3, lead accumulations over the 34 to 48 year period were related to the density of motor vehicle traffic in the surrounding area. Since sampling sites were well removed from highways, and deeper soils showed no increases above 20 mg Pb/Kg, the lead increase at the surface had undoubtedly been carried to and deposited on the land as aerosols.

Table 3.–Accumulations of Lead in the Surface 2.5 cm of Soils as Related to Motor Vehicle Density*

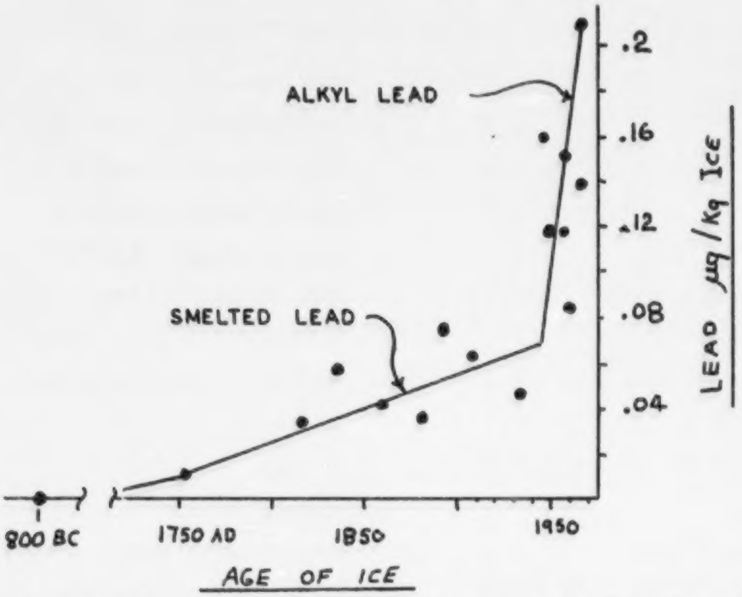
	Lead Content mg/Kg		
Location	1919–33	1967	Vehicles /Sq. Mi.
La Verne	17	52	735
Puente	16	52	1525
Whittier	16	39	2475
La Habra	17	50	1475
Tustin	16	31	1370
Riverside	17	38	580
San Bernardino	12	24	630
Hemet	19	21	25
Santa Paula	21	23	80
Meloland	26	25	50

* Source: Page, A. L. and Ganje, T. J., Accumulations of Lead in Soils for Regions of High and Low Motor Vehicle Traffic Density, Environ Sci and Tech 4:140, 1970.

Lead is also found in large amounts in rain waters! Six metals: Pb, Zn, Ca, Fe, Mn and Ni, were tested by the National Center for Atmospheric Research *(22)* in 1966-67 at 32 collection stations across the U.S. The lead in rain water correlated well with gasoline consumed in that collection station's area. The authors state, "Only lead is significantly high with respect to allowable concentration in drinking water."

In 1968, Murozumi, Chou, and Patterson *(23)* published results of four years of corroborative geochemical research on snows (1964-1968) under the title *Chemical Concentrations of Pollutant Lead Aerosols, Terrestrial Dusts, and Sea Salts in Greenland and Antarctic Snow Strata.* This extraordinary 106-page document gives the minute details of how snow blocks and melting operations were conducted to avoid lead contamination. Figure 6 shows how lead has accumulated in Greenland snows from 800 B.C. to 1964. The authors stated that "Industrial lead aerosols which were removed from the atmosphere by polar snowflakes originated mainly from smelteries before 1940 and from burned gasoline after that date."

Fig. 6. Lead in Greenland Glacial Ice *



* *Chemical Concentrations of Pollutant Lead Aerosols, Terrestrial Dusts, and Sea Salts in Greenland and Antarctic Snow Strata*, M. Nurozumi, Tsaihwa J. Chow, and C. Patterson.

What does it all mean?

While lead accumulations in remote California soil, in rain waters across the United States and in snows of far-off Greeland may seem unrelated to any medical questions of potential toxicity due to airborne lead, they do suggest rather widespread environmental diffusion of what must be tremendous quantities of a well-known poisonous metal. In the U.S. alone in 1970 we added nearly three pounds of lead per capita to gasoline, of which over one pound will be spewed from tailpipes into the atmosphere as aerosol lead! Although it is not possible at this time to answer the questions raised by Patterson, Schroeder and Tipton, Danielsson, and others about a) chronic lead insult, b) innate toxicity, and c) chronic tissue damage, there is no doubt that our urban air contains 100 to 1000 times more lead than that found on remote mountain tops or over the Mid-Pacific. For the city dweller who must continuously breathe 1 μg Pb/m^3 to 10 μg Pb/m^3 every day of his life, the question of an increased lead burden is no longer a theoretical or academic question. For example, Table 4 gives the last quarterly (October, November, December of 1970) composite data available for 39 sampling sites in Connecticut. For comparison, the California Air Resources Commission recently set 1.5 μg Pb/m^3 as the California standard not to be exceeded!

Table 4. Lead in Connecticut air (μg Pb/m^3)
4th Quarterly Composite for 1970

Ansonia	3.5	New Britain - Herald	6.1
Bridgeport	2.8	New Britain - City Hall	6.0
Danbury	4.4	New Britain - Mid A	4.0
Fairfield	0.9	New Britain - Pulaski	2.9
Greenwich, Cos Cob	2.4	New Britain - Smith S	3.2
Greenwich, T.H.A.	2.4	New Haven - Clinton	4.9
Greenwich, Byram	4.1	Norwalk - A.S.C. Bldg.	7.5
Greenwich, Witherall	2.5	Norwalk - Health Dept.	7.6
Groton	2.1	Norwich	3.4
Hartford Library	2.7	Orange	1.7
Mansfield	0.8	Putnam	3.5
Middletown City Hall	2.7	Stratford - Bunnell H.S.	3.3
Middletown Moody School	0.4	Stratford - Stratford H.S.	6.2
Milford - H.S.	2.8	Thomaston	2.9
- Devon	2.6	Thompsonville	2.8
- Eels Hill	0.7	Torrington	0.5
Morris	0.6	Waterbury	3.8
Naugatuck	1.2	Winsted	0.4

I often wonder if the inner-city child poisoned by eating leaded paint from an old building may not have a lesser margin of safety today than in former years, simply because his body has equilibrated with the significant amounts of lead found in city air. The study presently in progress with Dr. Martha Lepow of the University of Connecticut School of Medicine, comparing rural poor and urban poor children, strongly suggests that this is a factor.

Environment Lead - An Indicator of Little-Recognized Interactions Between Highways and Public Drinking Waters

The Roadside Environment

Highways--especially roads carrying ten's of thousands of vehicles each day--cause major transformations of our country's topography. While gross disruption of geological features is easily recognized, the profound changes in adjacent soil, air and water quality are difficult to access. It is becoming increasingly clear that secondary effects caused by construction, maintenance, and massive vehicular use of highways, must receive greater attention and deliberate study. Even cursory examination of highway roadsides show they are not the places of beauty and lush plant growth of former years. The accumulated residues of dirt, dust, sands, salts, trash, tars and strange exhaust odors intuitively suggest to the thinking individual that the sooner he leaves this roadside locus, the better.

In addition, what no one can "see" without the aid of laboratory measurements is the indivisible build-up of chemical substances which have silently accumulated well in excess of the natural background levels in the major roadside environments. The chemical data which are available mainly by measuring lead suggest that this roadside environment now extends laterally from highways for distances of several hundreds to 2000 feet. *(8) (20) (21) (24) (25) (26) (27) (28)*

Isolation of drinking water supplies

Until very recent times one of the primary protective mechanisms for public drinking water supplies in Connecticut was isolation and control of watershed lands and reservoir waters. The one major exception to this sound public-health policy seems to be roads.

With completion of the Connecticut Turnpike (I-95) in the early 1960's, about fifteen Connecticut public reservoirs are now crossed or encroached upon by highways, as shown in Table 5. Perhaps the reservoir most encroached upon by a highway(s) is the New Haven Water Company's Beaver Brook Reservoir in Milford, Connecticut, with watersheds crossed by both the Boston Post Road (Route 1) and the Connecticut Turnpike (I-95). The historical record of chloride build-up in Beaver Brook Reservoir (see Table 5) is remarkable, going from 2.8 mg Cl/l in 1900, 5.1 mg Cl/l in 1930, 23 mg Cl/l in 1962 to the highest in the state for surface waters, reaching an average of 47 mg Cl/l in 1969. These changes should speak for themselves, since it is obvious that as a result of the use of de-icing salts spread on the roads most of this chloride was either washed directly off the highways or leached from the adjacent roadside soils.

A more striking example of a highway's interaction with public drinking water supplies is Farmington's Wadsworth Reservoir which receives

Table 5. Connecticut Reservoirs encroached by highways

(Chloride Build-up since 1900)

Town	Utility	Reservoir	Highway	CHLORIDES * (mg Cl/1 water)			
				1890-1900	1930	1962	1969
Branford	N. H. Water Co.	Saltonstall	Rt. I-95	3.7	5.2	10	16 (Parathione)
Bridgeport	B. Hyd. Co.	Aspetuck	Rt. 1o6	---	---	--	--
"	"	Hemlocks	Rt. 136	3.7	3.9	8	12
Bristol	B. Water Dept.	Bristol #1	Rt. 6/202	(2)	2.7	--	12
Farmington	F. Water Co.	Wadsworth	Rt. 6	1.8	2.9	--	38
Greenwich	G. Water Co.	Putnam	Merrit	(3-4)	---	--	9
Groton	G. Water Co.	Groton	Rt. I-95	(3-5)	5.9	--	15
Hartford	M.D.C.	Nepaug	Rt. 4	(2)	1.8	5.2	5.0
Hartford	M.D.C.	No. 1 (not used)	Rt. 4	1.7	4.7	--	(23)
Meriden	M. Water Dept.	Broad Brook	Rt. 68	1.9	3.5	--	10
Middleton	M. Water Dept.	Mt. Higby	Rt. 66	2.5	3.5	--	18
Milford	N.H. Water Co.	Beaver Brook	Rt. 1 & I-95	2.8	5.1	23	47
New Haven	N.H. Water Co.	Whitney	2 town roads & Rt. 10A	3.0	6.0	10	12
New Haven	N.H. Water Co.	Watrous	Town roads	(3-5)	4	--	12
Stonington	Mys. Valley Water	Palmer	Rt. I-95	5.1	4.8	--	15 (Parathione)
Wallingford	W. Water Co.	Mackenzie	Town roads	2-3	3	--	19

* Natural levels of water chloride in Connecticut go from 7 to 5 mg Cl/1 near the Long Island Sound to 1 mg Cl/1 at the Massachusetts-Connecticut boarder.

drainage from Route 6. On February 12, 1970 the West Hartford News printed on page 4 a letter from a lady in Farmington (E. Daphne Kennedy) reporting

> ....."The Farmington water had an unpleasant, oily taste; a greasy scum (which stained the cup) formed on the surface of tea or coffee. Discovering the town reservoir bordered Rt. 6, I decided run-off from the highway was the culprit.".....

On February 18, 1970 tests conducted by the State Health Department on Wadsworth Reservoir water showed 32 mg Cl/l (versus 2 mg Cl/l natural background levels); but in addition, even with the water pH at 7.1, lead was present at the concentration of 15 μg Pb/l ! This less soluble element, a known waste from motor vehicle exhausts, was appearing in what must be one of the highest concentrations yet recorded in raw surface waters in Connecticut.

Table 6 lists the lead found in surface waters for rivers and public water supplies as given in *U.S. Geological Survey Circular No. 643* for sampling in October 1970 *(28)*. Note that the 15 μg is an extremely high level--especially for a public drinking water supply. Of twenty-three reservoir sites listed in Connecticut and Massachusetts, only one reached 10 μg Pb/l and of the 25 samplings made in Connecticut only one reached 10 μg Pb/l (Connecticut River at Thompsonville). As shown in Table 6, the U.S. Public Health Standard for lead in drinking water of 50 μg Pb/l does not represent an adequate limit, based upon the observed facts, and 25 μg Pb/l is a more realistic upper limit for raw water. A 10 μg Pb/l limit on potable (processed) water would be more in keeping with what is actually being supplied!

I-291 - A Highway Through a Reservoir

Thousands of Connecticut citizens were amazed to learn in the West Hartford News in March 1969 that a major portion of their Metropolitan District Commission (M.D.C.) terminal water distribution and filtration system on Talcott Mountain would become "roadside" for I-291 and its daily 60,000 vehicles. The response was astounding, for within days 80-90% of the people approached in the 13th Connecticut State House District (the farthest removed from the M.D.C. lands in West Hartford) had signed a petition requesting Governor Dempsey to call a hearing. This soon reached 6,000 signatures and finally contained 10,000 names, including persons from every community served by the M.D.C. Water Bureau. Over 1,000 persons attended the hearing on September 25, 1970, and the recorded testimony--consisting mostly of objections--formed a 3-inch thick document. The spectrum of persons and organizations testifying was remarkable. It included private citizens, ecologists, social scientists, engineers, conservationists, and local government officials, as well as many persons representing medical and public health concerns. Subsequently both candidates for governor declared themselves against this routing of I-291

Table 6. Lead in surface waters of U.S.A.

Source: U. S. Geological Survey Cir. #643 (1970)

µg Pb/l	Frequency	% of Total	Accumulated %
< 1	279	38	38
1	59	8	46
2 (median)	66	9	56
3	56	8	63
4	55	8	71
5	51	7	77
6	19	3	80
7	18	2	83
8	12	2	84
9	13	2	86
10	20	3	89
11 (90%)	9	1	90
12	8	1	91
13	7	1	92
14	9	1	93
15	5	1	94
16 (95%)	3	< 1	95
17	6	1	95
18	1	< 1	95
19	1	< 1	96
20 - 24	13	2	97.5
25 - 29	7	1	98.4
30 - 39 (99%)	7	1	99.1
40 - 49	2	< 1	99.5
50 and above	4	1	100

near the public water supplies. Recently the 1971 General Assembly passed a bill specifically prohibiting the construction of I-291 in the M.D.C. reservoirs; but Governor Meskill, for poorly understood reasons, vetoed this--despite his strong campaign promises.

Rationale for 1/4-mile buffer zone

The major objections to the Department of Transportation's I-291 route through the M.D.C. lands was entered into public testimony by Mr. Woodhall, Chief, Water Supply Section, Connecticut State Department of Health, on reading a letter from Dr. Foote, Commissioner of Health in September 1970. This testimony recommended that no highway come within 1/4 mile of a public water supply in order to protect the water supply from accidental spills and other pollutants and wastes coming from the highways. This distance corresponds well to that at which the smallest lead particulate aerosols reach general background levels and thus would probably give some protection against gaseous substances as well. The Health Commissioner's timely recommendation to restrict encroachment upon reservoirs in Connecticut has been favorably received and endorsed by:

1. The Public Health Council
2. Connecticut Clean Air Commission
3. Connecticut Public Health Association
4. Connecitcut Air Conservation Committee (TBRD Assoc.)
5. Executive Council Connecticut State Medical Society
6. Governor's Task Force on Lead.
7. Glastonbury Water Commission and Town Council
8. (Indirectly) Governor's Environmental Policy Committee Report
9. Ninety plus local physicians (signed petition)
10. (By campaign promises) both candidates for Governor (Meskill and Daddario) as well as candidates for the Senate and House on both State and National levels.
11. Actions by town governments in Whethersfield, Windsor, Hartford and Bloomfield and West Hartford.
12. Connecticut's General Assembly (1971) Session.

Why this diffuse public support?

In the early 1960's there was not a great public outcry when I-95 was built across or adjacent to four coastal reservoirs (Beaver Brook Reservoir in Milford, Saltonstall Reservoir in Branford, Groton Reservoir in Groton, and Palmer Reservoir in Southington). At that time, the most state health department personnel could do was to work for proper isolalation of highway run-off. Now in 1969 and 1970 the public said "NO" in very unequivocal terms. Why this significant difference? Perhaps the reasons are due to:

(1) The widespread feeling today that environmental quality is deteriorating at a rate not matched by positive corrective steps.

(2) The general conviction that something must be done to improve air and water quality in Connecticut. (Certainly no one can justify to the public why drinking water should be placed at any risk.)

(3) The growing awareness of unexpected side effects from the use of chemicals or chemical waste byproducts (detergents, thalidimide, DDT, Hg, hydrocarbon, smog). And

(4) The increasing evidence, both locally and nationally, that Interstate Highways have not resolved our urban transportation needs, but have created major secondary problems (i.e. air pollution, social disruptions).

This articulate opposition to I-291 through the M.D.C. Reservoir lands demonstrates that the public is deeply concerned about the subject of environmental health. Prosperity and affluence are no longer sound goals if a health trade-off is required or even suspected. Basic biological needs must come first!

Future public policy regarding highways near reservoirs

The Department of Transportation planned encroachment by I-291 in the M.D.C. Reservoir lands in West Hartford, while momentarily halted, has convinced me of the need for a strong, aggressive public policy to protect and improve surface drinking-water supplies in Connecticut. Mr. Woodhall, in testimony on August 26, 1970 before the Joint Public Health and Safety Committee of the Legislature, has already taken some basic first steps when he called for (1) restrictions on the use of river waters for drinking, (2) filtration of all surface supplies, and (3) increased chemical monitoring of potable waters for trace elements (As, Cd, Cr, Pb and Hg) and complex organics such as hydrocrabons, pesticides and herbicides. At the same August 26, 1970 hearing, I recommended that the 1/4-mile buffer zone suggested by Dr. Foote be made law, with exceptions granted only after full approval of the State Health Department, the Connecticut Public Health Council, and the new Council on the Environment. I also testified that the present hazards created by highway encroachments on the fifteen existing reservoirs should be corrected for run-offs (i.e., Beaver-Brook, Wadsworth) and altered to eliminate reservoir crossings (Nepaug, Saltonstall) so that no tank or trailer truck spills could possibly enter the drinking water. These changes should be financed as first priority projects from the privileged Highway Tax Fund. These legislative moves would represent a positive step in upgrading one of the most essential needs of man: pure water!

A Timely Opportunity -
The study of highway reservoir interactions

The need for an objective technological assessment of these highway reservoir interactions cannot be overstressed. I suggested that the Connecticut Public Health Council and the Connecticut State Health Department, together with the U. S. Geological Survey branch office in Connecticut (perhaps even with the D.O.T. environmental sections or their national equivalent) initiate basic studies to gain the type of objective data needed to contribute to the solution of this complex problem. For example, M.D.C. Reservoir #1 is an ideal study site since this reservoir is no longer used for drinking water yet is adjacent to Route 4 with its 15,000 vehicles per day. As shown in Tables 7 and 8 from my measurements last year, studies should include local air, soil and plant life samplings on land, as well as measurements for numerous chemical elements on bottom sediments, aquatic plants and animal life. The easy contrast afforded by clean M.D.C. Reservoir #2, one-half mile to the west of M.D.C. #1, or dirty Wood pond, one-half mile east, which drains I-84 (or even Farmington's Wadsworth Reservoir on Route 6) would give a tremendous volume of information in a very limited geographical area near the central State health office for good administrative and laboratory control.

However, I am sure any study next to any large highway and adjacent water body will reveal many undesirable interactions. I suggest that our society's need is for basic knowledge of biological reality, which must be built upon observation. Armchair conjecture by "experts" with vested interests to protect and little understanding of the complex biological systems involved will fail to see the multiplicity of interrelations.

We have a unique opportunity for a new insight. The environmental quality frontier is right wherever we are, and the clinical chemist can and should be out exploring!

SUMMARY

As a nation, we have hardly begun to study the effect of trace metals in our environment. Work with lead over the past few years supports the concept that occult or innate toxicity may be quite common. There is a critical need for continued improvement in clinical blood lead measurements to help define more clearly the significance of values between 30 to 50 μg Pb/l WB. We should be deeply concerned as biologists and chemists about the effect of this toxic element - lead - which is continuously being released into the environment in ever-increasing amounts.

In an article entitled, *Taming Technology (29)*, Dr. Branscomb, Director of NBS, points out that we must use the full power of science to understand the problems created by our technology and to bring about governmental policy "based upon the rational consideration of the scientific facts in their social context." Scientists must become environmental activists--the clinical chemist can be no exception--if rational public policy based upon biological and chemical reality is to prevail.

Table 7. Lead in bottom soils of reservoirs

DATE	PLACE	WATER DEPTH	LEAD VALUE µg Pb/gm dry soil
9/28/70	Clean - MDC Res. No. 2 NW corner Dyke Pond	6 inches	45
10/ 1/70 *	Clean - MDC Res. No. 2 SE along Dyke Pond	6 "	28
9/28/70	Road - MDC Res. No. 1, 10 feet east Route 4	6 - 12 inches	237
9/28/70	Road - MDC Res. No. 1, 50 feet east Route 4	6 - 12 "	138
10/ 1/70 *	Road - MDC Res. No. 1, 10 feet east Route 4	36 inches	320 **
10/ 1/70 *	Road - MDC Res. No. 1, drain west of Route 4	6 inches	180
9/28/70	Clean - MDC Res. No. 6, SW end	3 inches	32

** Cadmium 10 µg/gm dry soil

Table 8. Lead in ash of plantlife in reservoirs

DATE	PLACE	PLANT	LEAD VALUE µg Pb/gm dry soil
9/28/70	Clean - MDC Res. No. 2, NW corner Dyke Pond	Myriophyllum (milfoil)	105
10/ 1/70 *	Clean - MDC Res. No. 2, NE corner Dyke Pond	" "	240
9/28/70	Road - MDC Res. No. 1, 10 feet east Rt. 4	" "	990
9/28/70	Road - MDC Res. No. 1, 10 feet east Rt. 4	floating algae	360
10/ 1/70 *	Road - MDC Res. No. 1, 10 feet east Rt. 4	Myriophyllum (milfoil)	600
9/28/70	Road - Ely Pond, S Route 44	" "	360
9/28/70	Road - Welles Pond, S and draining Rt 44	(unknown)	720

* These samplings and identifications were made with the help of Mr. Woodhall, Connecticut State Health Department; Mr. Minkus, Metropolitan District Commission; Miss Priscilla Christman, Graduate School Yale University.

The degree to which man--particularly in affluent Western society--has contaminated the Northern Hemisphere's air, waters and soils with alkyl leads since 1923 is little recognized by most individuals. Similar to the story with pesticides, herbicides, oil spills on the oceans, and the newly-evolving story of polychlorinated biphenyls and mercury, we are now recognizing that technological advances may actually result in major disruptions of ecological systems vital to man. What possible ecological nightmares we have created for living organisms by burning alkyl leads so wantonly for the past fifty years is as yet unknown. It is clear, however, that man himself, because of the efficient filtering action of his lungs, has not escaped an ever-increasing burden of lead, a toxic metal. As Patterson, Schroeder and Tipson, and Danielsson suggest, we are probably paying a biological price which we have as yet not learned to recognize.

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AUTOMATION AND COMPUTERIZATION OF ANALYTICAL MEASUREMENTS

J. R. DeVoe

Abstract

Design of computer systems for assistance in the operation of experiments contains certain factors unique to a particular laboratory. Details are given on the procedure used to generate design criteria and to implement such a design for a computer system in the Analytical Chemistry Division, National Bureau of Standards.

Key Words: computer, digital communication system, laboratory automation, multi-program monitor.

CONSIDERATIONS IN THE DESIGN OF THE SYSTEM

In this period of ever-increasing emphasis on automated (machine operated) equipment, great care must be taken to be assured that the computer as used in the research laboratory is indeed an assistance and not an all consuming task that slowly erodes proper orientation. It is perhaps obvious that design of a computer system for any given laboratory contains certain factors unique to that laboratory. Certain aspects of the design can be formulated to accommodate most of the needs, but there are no magic formulas to be applied for those remaining. Indeed, the procedure for obtaining design of a good computer configuration is similar to that for the design of good experimental apparatus.

To be sure, the variables to be considered can be described in some detail as is done below, but the determination of proper weight to be attached to each one requires great care and deliberation. There are some factors not described subsequently, and these should be mentioned. Designing a computer system depends upon the type of laboratory, mission, (research, development, production, etc.) and the personnel available.

In the educational institution it is necessary and desirable that students have experience with computer programming in assembly language and that they learn the fundamentals of computer operation. This is not the case in our division at NBS where professional analysts must devote full time to developing measurement methods of great accuracy, and have little time for programming.

There is no question that assistance from a computer specialist is always necessary. A major problem that exists in all systems design is the availability of appropriate people who understand the needs of scientists as well as the capabilities of the computer and programmers for satisfying these needs. Without such people, communication between programmers, electronic engineers and the scientists breaks down and all is lost.

The following paragraphs describe an approach toward automating an entire laboratory in which programming of the computer is done by experts, and the running of the experiments with the assistance of a computer is done strictly by the analysts themselves.

Design Criteria for Laboratory Automation in the Analytical Chemistry Division of NBS

The very first task--after it has been decided that computer interaction with analytical instrumentation is a reasonable thing to do--is to determine the operational requirements.

Representatives from each section in the division formed an Ad Hoc committee to generate some feeling for the requirements of the division, and to provide several suggested paths which could be taken to fulfill the requirements.

The requirements are as follows:

General: The goals are of two categories. First is a data acquisition system that will cause data to be stored, computed upon and answers formulated and disseminated to the site of the experiment. Second is an experiment control mode which provides a computation of acquired data and as a result generates control functions to modify input parameters to the experiments (such as temperature programming, time rate of change of potential in electrochemistry, etc.).

Specific requirements (with respect to the general requirements) are as follows:

1. Experiments should be able to utilize the computer day or night. The analyst at the instrument should be able to initiate computer interaction. Appropriate communication should be easily performed. Approximately 50 experiments should be able to utilize the computer under the above conditions at any time.

2. Types of experiments (divided into major classes--the number of instruments are given in brackets).

   a. Spectrophotometer, Visible, UV, IR, [8].

   b. Chromatographs [8].

   c. Multichannel analyzers and/or small computers, e.g. used with NMR, gas phase mass spectrometry, electron microprobe [10].

d. Temperature programming (pH measurement, electrochemistry, gas chromatography, DTA, etc.) [6].

e. Miscellaneous instruments having digital readout capability; x-ray fluorescence [2], carbon analysis, coulometry, flame emission spectroscopy, atomic absorption spectroscopy, differential scanning calorimeter, etc. [10].

f. Miscellaneous devices having only analog signals, e.g. driving strip chart records. Thermogravimetric analysis, gas mass spectrometer, polarograph, other [10].

g. Several instruments qualify under more than one of the above categories, such as the microprobe analyzer [4].

3. Data rates vary over a wide range. Buffered data (4,096 - 6-digit numbers) can be read at any reasonable rate. Other non-buffered data must be read at from an extreme of 10,000 - four-digit numbers per second for not more than 30 seconds to a few numbers per minute.

4. Archive files for the various experiments should be available which allow retrieval of data upon request.

5. Response times for generating control signals to an instrument should be from a minimum of a few milliseconds to a maximum of several minutes.

6. Responses to the experiment should be of two types: one is to provide analog signals (resolution of 1 to 0.1 parts per 1,000) for adjusting independent variables on the instruments and to provide contact closures for turning on and off various experimental variables; the other response is to provide results in the form of data and/or graphic displays at the site of the experiment.

7. Data should be able to be properly formatted for entry into a large computer for processing. An interactive console should be available to allow the analyst to manipulate experimental data with or without lengthy computations.

8. The system must include backup which takes over data acquisition for some experiments if the system goes down.

Based upon these requirements, several manufacturers advised us to consider rather large computers, but all of these were out of the question because of cost. The division's Ad Hoc committee recommended to the Division Chief four alternatives. Alternative I was to connect small computers (4-8,000 words - 12 or 16 bits/word) to each experiment or series of two or three experiments. This is expensive, although costs now are reducing rapidly. Moreover, in the absence of convenient data links to a large computer for the purpose of storing data and file manipulation, a number of costly large-volume data-storage devices would be

Alternative II was to use the system in Alternative I on a large computer remote to NBS. However, current and/or five-year projected response times combined with high cost negated this possibility. Alternative III utilizes a medium-sized machine (32,000 words - 16-19 bits/word). In retrospect, this has the least number of disadvantages; but at the time, it appeared that the cost would be too high. Alternative IV was the large computer, and as indicated above, it was rejected.

The Ad Hoc committee suggested Alternate I or II and a Computer Procurement Committee was formulated to arrange for purchase of a small computer system. It is important to describe the formation of this committee, since it embodied the backbone of the entire system and provided the mechanism for the interdisciplinary communication described above. The committee was comprised of two electronic engineers, Ronald W. Shideler and Fillmer C. Ruegg, who have considerable experience in nuclear and digital electronic applications; one system analyst, Roy G. Saltman, from the NBS Center for Computer Services and Technology (CCST) who is experienced in laboratory automation; and two analytical chemists, Stanley D. Rasberry and the author, who have experience in a variety of spectroscopies and utilization of computers.

Specifications for the computer system were written by Roy Saltman of the CCST. Briefly, the request for proposal contained specifications for two computers. One was to be a free-standing small computer that could be moved into a laboratory to set up control of an experiment. At the end of the prove-in, a small computer would be purchased to replace the set-up machine. The other small-to-medium-sized computer was to acquire data from experiments and time-share storage devices. The specifications reflected the requirements indicated above.

At this time a digital data communications system was formulated and designed by R. Shideler, with assistance from F. Ruegg, to provide communication between the experiment and the time-shared small computer.

Response to our request was surprising. Many manufacturers felt they could meet the hardware requirements; but few had the proper monitor to time-share storage of data. Several companies did have reasonable starts on a monitor, and the computer finally obtained proved to have superior software. The existence of this medium-sized computer system caused a revision in part of our plan. It is possible that only a few additional small computers will now be required to fully implement the most important of the Division's requirements.

It is believed that all of the Division's requirements will be met via the system to be described, except response time at or below one millisecond and the interactive console. These will require another small computer (each) attached to this system.

GENERAL DESCRIPTION OF THE DIGITAL DATA COMMUNICATIONS SYSTEM

Introduction

The data communications system consists of four main parts: (1) the digital data bus, (2) the computer interface, (3) the laboratory interface, and (4) the experiment control panel. The computer interface connects the computer to the laboratory via the digital data bus and laboratory interface. The experiment control panel provides the capability of entering auxiliary data for use by the computer at the location of the interface. The following section was written in part by Fillmer C. Ruegg, Analytical Chemistry Division.

Philosophy of a Digital Communications System

At the start of designing a system for data communication, one must ask: How will we do it?--analog or digital? It was felt that a digital system offers many advantages over an analog system for data transmission, because of the inherent noise rejection qualities of digital communications systems. Another important reason for taking the digital approach is the recent drop in the price of analog to digital (ADC) and digital to analog converters (DAC). However, we are keeping some analog capability with the addition of a multiplexed ADC at the computer.

The Digital Data Bus

A party-line digital data bus has been installed in the chemistry building, with an outlet for each laboratory (see Figure 1). The data bus has 50 individually-shielded twisted pairs of wire. The data will be transmitted from the laboratory interface to the computer interface using differential drive and sensing so that common mode noise induced on the twisted pair will be canceled. The data bus will be divided as follows: (1) Pairs 1 through 8 will be used as the interfaced machine's address, (2) Pairs 9 through 25 for first 16 bits of data plus parity, (3) Pairs 26 through 42 for second 16 bits of data plus parity, (4) Pairs 43 through 50 for control signals.

The communications between the laboratory and the computer interfaces will be accomplished with a multilevel time multiplexing scheme. To achieve the first level of multiplexing the data producing devices were divided into two classes: (1) Buffered data which can be transferred at speeds between 1,000 double precision 16-bit words per second and 50,000 double precision words per second; for example, multichannel analyzers. (2) Non-buffered data which will be transferred at rates less than 1,000 double precision words per second, i.e. digital voltmeter, scaler-timer, etc. The two types of data are time multiplexed onto the party line bus by a square wave clock, with the high speed buffered data going onto the lines when the clock pulse is the most positive voltage and the low speed non-buffered data being entered when the clock pulse is the most negative voltage.

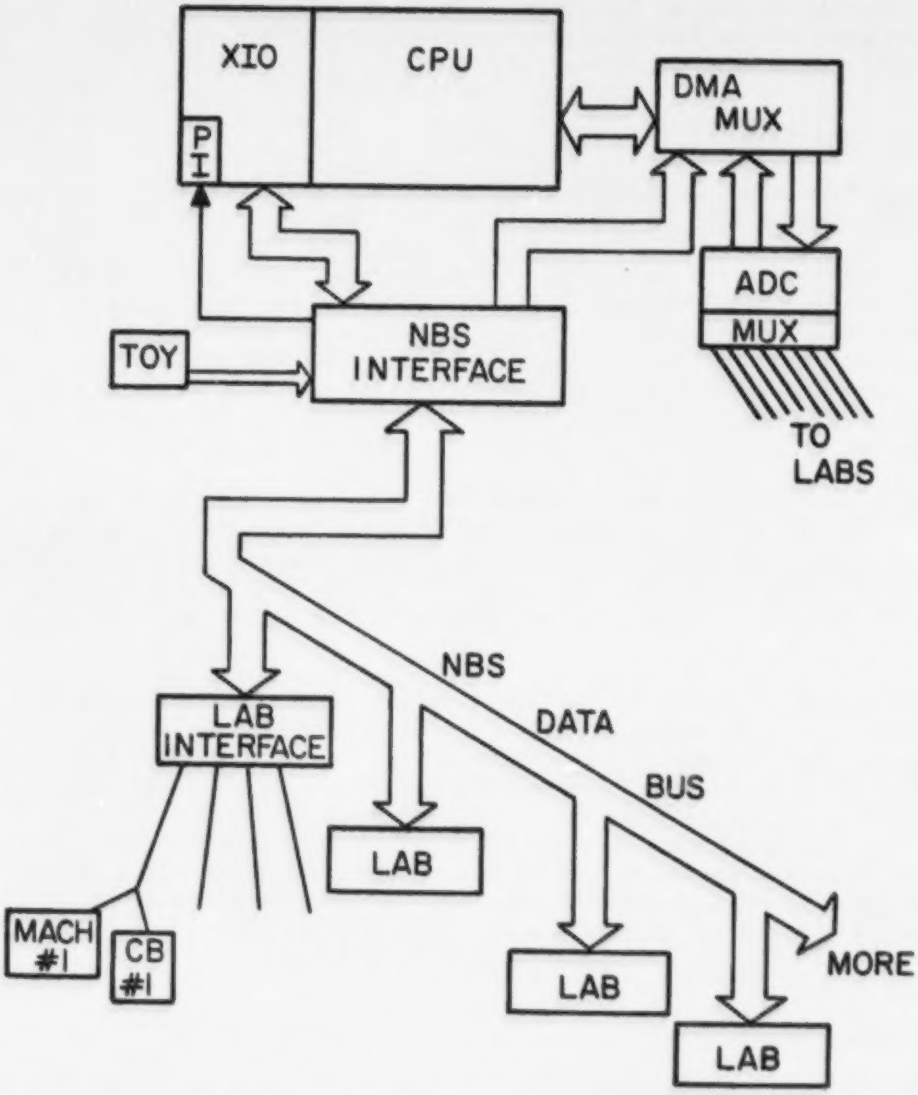

XIO
CPU
P
I
DMA
MUX
ADC
MUX
TO
LABS
TOY
NBS
INTERFACE
NBS
DATA
BUS
LAB
INTERFACE
LAB
LAB
LAB
MORE
MACH
#1
CB
#1

Figure 1. Data path for Analytical Chemistry Division computer system.

The next level of multiplexing was added to determine which low speed machine could enter data onto the bus. This was achieved with the addition of a low-speed intercept pulse which is transferred from laboratory interface to interface in a circular pattern, passing through the computer interface on each trip around. The interfaces have the capability to capture this pulse when it arrives at their location, and while the pulse is captures, the interface can enter data onto the bus during the low-speed side of the clock. The high-speed side of the clock is assigned to one and only one laboratory interface at a time by the computer on a demand basis.

The Computer Interface

The computer interface contains the necessary logic circuitry to interface the digital data bus to the computer. The interface also is connected to a time of year clock which can enter the time with the data which is received from the laboratory. The computer interface must separate the high-speed and low-speed data and assemble the forty bits of received data into computer length words in the proper sequence. The high-speed words are sent to the computer through the DMA part of the interface. The low speed words are transferred to a ripple shift register where they produce an external priority interrupt and are read in by the computer.

The computer interface also accepts data from the computer to be sent back along the bus as an output. The computer provides an address and either a single or double precision word which the interface assembles into the format used on the bus and sends the output data on the data bus to the proper laboratory interface and thence to the proper machine address.

The other main function of the computer interface is to maintain a constant check for malfunctions of the digital communications system. One of the important checks is the parity of the incoming address and data words. If there is an address parity error, the address and data are not transferred to the computer, but the address is stored and displayed by the computer interface, and an alarm is sounded which must be reset by the computer operator. If either of the data words has a parity error, the data will be sent to the computer but the computer will be informed of the parity error, and an alarm will be sounded and the address from which the data originated will be displayed.

The Laboratory Interface

The laboratory interface contains the logic circuitry necessary to connect up to four machines to the digital data bus. The laboratory interface is designed as a general purpose unit which will interface to almost all laboratory instruments. The laboratory interface will be able to supply a diverse number of outputs to the experiment from the computer.

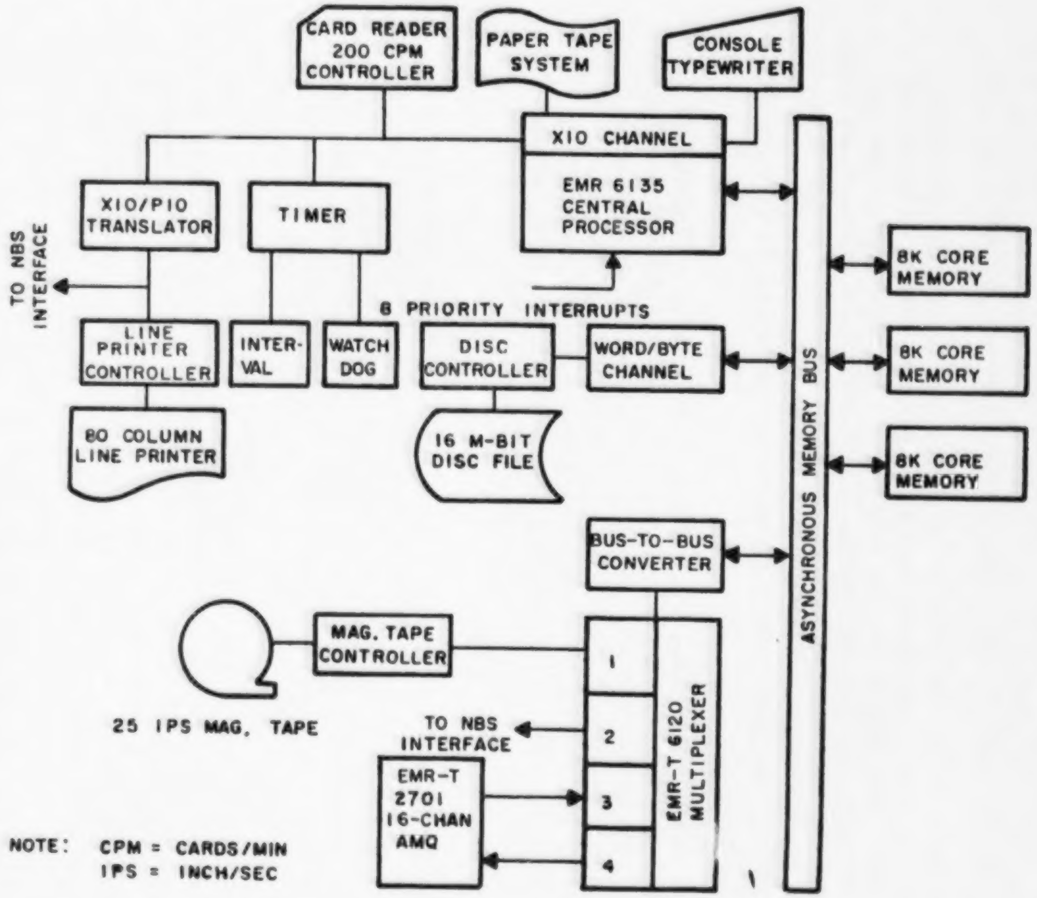

CARD READER 200 CPM CONTROLLER
PAPER TAPE SYSTEM
CONSOLE TYPEWRITER
XIO CHANNEL
EMR 6135 CENTRAL PROCESSOR
XIO/PIO TRANSLATOR
TIMER
TO NBS INTERFACE
8 PRIORITY INTERRUPTS
LINE PRINTER CONTROLLER
INTER-VAL
WATCH DOG
DISC CONTROLLER
WORD/BYTE CHANNEL
80 COLUMN LINE PRINTER
16 M-BIT DISC FILE
8K CORE MEMORY
8K CORE MEMORY
8K CORE MEMORY
ASYNCHRONOUS MEMORY BUS
BUS-TO-BUS CONVERTER
MAG. TAPE CONTROLLER
25 IPS MAG. TAPE
1
2
3
4
EMR-T 6120 MULTIPLEXER
TO NBS INTERFACE
EMR-T 2701 16-CHAN AMQ
NOTE: CPM = CARDS/MIN
IPS = INCH/SEC

Figure 2. Block diagram of computer.

DESCRIPTION OF THE COMPUTER

The configuration in Figure 2 shows the various components of the system and where the digital data bus connects. The magnetic tape deck is slow speed, high density. The disc is fixed-head with 1-million (16 bit) word capacity. The line printer and card reader are small ones provided for de-bugging programs. The basic clock us 7 MHz and a parity and memory protect bit are carried throughout the central processor and memory. A memory read or write time requires about 500 nano-seconds.

The software is in the form of an operating system called ASSET which partitions core into three dynamically-sized areas; foreground houses routines that assist in the running of the experiments and can be passed from core to disc as needed, middleground is the same as foreground, except that a program in this area has no memory protection. This assists in de-bugging of experiment routines without adversely affecting other foreground routines currently assisting in running of experiments.

The last area is the batch processor which houses a FORTRAN IV compiler and does mathematical computation on data collected previously. The ASSET system can select any one of these areas for execution on a short-time scale, so that they can be considered to be processing at the same time. In the event of inadequate space in the computer's memory, the priority for relinquishing core is background first and middleground second. Core is reallocated whenever a new foreground program is initialized or ended.

The computer has provisions for two types of inputs to memory: one called direct memory access (DMA), and one called the external programmed input-output (XIO/PIO). An initial interrupt starts a program which sets up a table in core and then returns to the interrupted work. The DMA type of input which is a direct transfer of information by stealing computer memory cycles is then started. This method does not disturb any of the central processor unit's (CPU's) registers so that the operation of the CPU is not affected in any way other than it being slowed. An XIO/PIO demand causes an interrupt which terminates the CPU's present program and starts a programmed routine which handles the interrupting device's needs, i.e. reading in data from cards, etc. When the interrupting device has been satisfied, the computer returns to the previous program that is left and continues to work upon it.

GENERAL DESCRIPTION OF SPECIAL SOFTWARE

Even though the monitor came with the computer in an essentially complete state and in operation, it is always necessary to write (in assembly language) those routines that are unique to the system. These routines were written by J. Aronson, R. Freemire, and B. Leong Hong of the NBS Center for Computer Sciences and Technology. The major effort centered about a routine that would handle data to and from the digital communication system. This is a general routine that handles all data and resides external to the normal operating system. This was done in order to minimize response time of the computer for getting data from the digital communication system. No time is lost within the monitor because this demand has the highest available priority.

Routines that control experiments can be written, compiled and executed from FORTRAN; however, it is often desirable to have accomplished language in order to conserve space in foreground. Data collected from these routines in foreground can be passed to FORTRAN routines that are run in background. The remainder of this section was written in part by Mr. Aronson and is a preliminary writing of part of the data acquisition routines.

The data acquisition routine called DACQ is written in assembly language, and there are two subroutines, DATA and CONN, that provide the link between the data acquisition program, DACQ, and the user programs. These also allow interconnection via FORTRAN call statements.

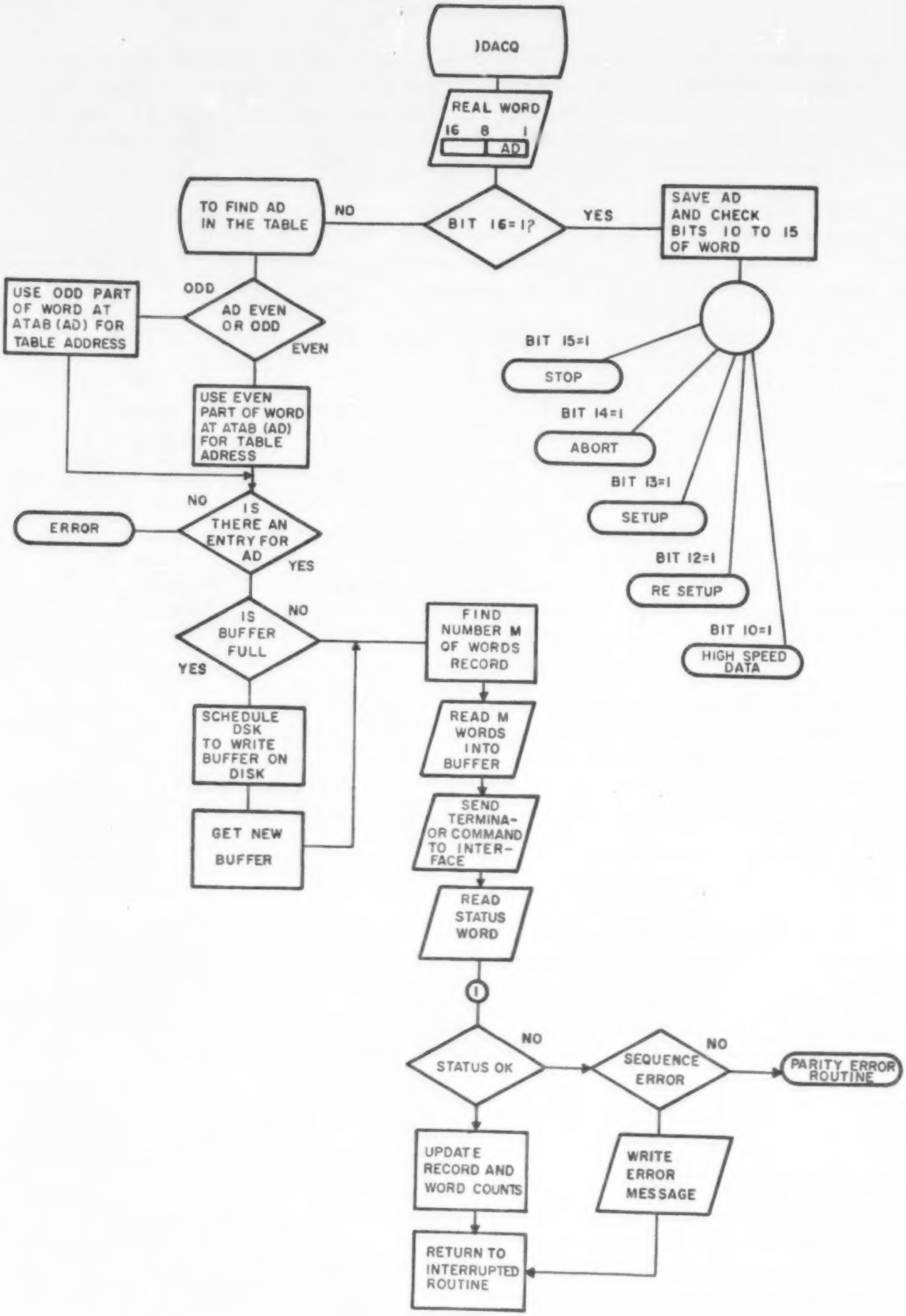
The routine CONN connects the users' program to DACQ so that after the receipt of each data record, his program is entered at a specified point. DATA is an input subprogram. By writing CALL DATA (X,n) the n'th data record is transferred to the array X in EBCDIC format. He can then use the DECODE statement to translate the record according to standard format statements.

The user need not be concerned with the operation of DACQ unless he has a control routine that requires very rapid response. His program will not be run immediately after the data record was sent. Instead, it is scheduled by a monitor called ASSET IV in a software priority system. That is, a request to run his program is put into a queue in the order of his priority. The queue is serviced in this order, and ties therein are decided on a first-come first-served basis. Very rapid response routines will be given highest priority.

The priorities assigned to the programs are of two types: hardware interrupt and software. The hardware priorities are higher than the software priorities. DACQ is assigned the highest hardware priority, while the other programs are assigned software priorities. The user's program will have a lower priority than those of the system. This was done to minimize the possibility of being unable to receive data from the laboratory device.

DACQ

DACQ receives and interprets control words from the computer interface to the laboratory digital data bus and transfers data words to the appropriate buffer (see Figure 3). It also causes user-supplied routines to be scheduled upon the receipt of each data record or at the end of the experiment. Data may be temporarily stored in a disc file from which it may be processed according to the user's direction.



)DACQ
REAL WORD
16 8 1
AD
BIT 16=1?
NO
YES
TO FIND AD IN THE TABLE
SAVE AD AND CHECK BITS 10 TO 15 OF WORD
ODD
AD EVEN OR ODD
EVEN
USE ODD PART OF WORD AT ATAB (AD) FOR TABLE ADDRESS
USE EVEN PART OF WORD AT ATAB (AD) FOR TABLE ADRESS
BIT 15=1
STOP
BIT 14=1
ABORT
BIT 13=1
SETUP
BIT 12=1
RE SETUP
BIT 10=1
HIGH SPEED DATA
NO
IS THERE AN ENTRY FOR AD
YES
ERROR
IS BUFFER FULL
NO
YES
FIND NUMBER M OF WORDS RECORD
SCHEDULE DSK TO WRITE BUFFER ON DISK
READ M WORDS INTO BUFFER
GET NEW BUFFER
SEND TERMINA-OR COMMAND TO INTER-FACE
READ STATUS WORD
1
STATUS OK
NO
SEQUENCE ERROR
NO
PARITY ERROR ROUTINE
UPDATE RECORD AND WORD COUNTS
WRITE ERROR MESSAGE
RETURN TO INTERRUPTED ROUTINE

Figure 3. Flow chart of data acquisition routine.

DACQ is a priority interrupt response routine. Upon receipt of a hardware priority interrupt from the computer interface, DACQ reads one word and interprets whether or not the record contains data. If it does, the address of a row in a table that contains experimental parameters (set-up words) is determined. From that row the number of words per record, buffer address and subroutine linkage are obtained. The data are then read into a buffer. Should that buffer be full, they are written on a disk file and a new buffer is obtained from a buffer pool.

The number of data records obtained from the setup words for the experiment is compared to the cumulative number of records. When the latter equals the former, the data acquisition is terminated. Further processing may then be done under the batch mode by a user-supplied program.

A non-data record may be either a control record for stop, abort, or high-speed data input, or one of the parameter records: setup, resetup. The indication of the type of non-data record is provided by bits 10 to 15 of the first word, e.g. high speed data, resetup, setup, abort, and terminate.

DACQ calls the following subroutines: SETUP, HSP, GETB, and DSK.

DSK

DSK writes a group of data records for one experiment onto the disk. It is called by DACQ when the buffer in core becomes full.

DSK writes the contents of the buffer, generally 50 words, onto a disk file. The first word of the written record will contain a pointer that links the record with the next record for the experiment. The table in DACQ will contain the record number of the first record for each experiment that has data on the disk. Thus, it will be possible to retrieve all records for each experiment.

SETUP

SETUP receives the setup words from the computer interface and makes entries into the DACQ table. The setup words contain the following parameters: the number of words per data record, the number of data records to be read, the program number of the applications director program, and the high speed indicator. The application director contains the control program for the experiment, and a batch statement which directs the batch processor to run a designated program or programs after the data have been completely read.

The number of words per data record and the number of records are entered directly into the row of the DACQ table that corresponds to the laboratory instrument ID number. Next the application director program is loaded and run. If there is a CONN statement, the entry address specified in that statement is entered in the DACQ table. The batch statement is read after all data for the experiment have been read. Then the batch processor directives are generated and written into the batch system input disk file.

CONN

CONN causes an address to be entered into the DACQ table, after which every time a data record from this experiment is received, control is transferred to the specified entry point. For example, CALL CONN(A), where A is a name of an entry point to a subroutine, causes the address of A to be stored in the appropriate row of the DACQ table. CALL CONN ($N) where N is a FORTRAN statement number causes the address of that statement to be stored in the table.

DATA

DATA transfers a data record to an array and converts the data to EBCDIC characters. EBCDIC is used to permit the data to be converted directly by Fortran DECODE and FORMAT statements.

The statement CALL DATA(X,n) transfers the n'th data record to the array X and increments n by 1. For example, if each record consists of a six-digit number with an implied decimal point after the third digit, the following statements will transform the number to a floating point form:

```
             CALL DATA(X,n)

             DECODE (6,1000,X)A

        1000 FORMAT  (F6.3)
```

HSP

This program reads the data over high-speed lines into a buffer from which it is then transferred to a disk file. HSP is called by DACQ when the first word of the low speed record has bit 16 and bit 10 set.

The number of words to be read are calculated from the DACQ table. Next the ASSET routine, RMS, is called to get storage for a buffer. RMS returns only after the storage is available. The multiplexer subchannel is then initialized. When the data have been read, an interrupt will be generated by the multiplexer which ultimately causes a jump to the completion part of HSP. There the data are transferred from the buffer to the disk file.

Data Processing Routines

This operating system has the capability of processing data in background mode. These programs are written in FORTRAN and assistance is being given to the analyst to provide for this type of data processing. Considerable effort has been expended to determine what basic or common subroutines can be written which many analysts will want to use.

The generation of averages and standard deviation plus fits to a straight line are obviously needed. These routines are available and considerable documentation will accompany them. In addition, a study is being made to determine how much can be done for spectroscopists in resolving peaks.

Additional routines will be written to format data for transmission to the NBS Univac 1108.

OPERATION OF THE SYSTEM

Assume that you are an analyst at your instrument prepared to run an analysis with assistance from the cmputer. Your operating procedure is as follows: (See Figure 4, the operating panel). A blue ON light is illuminated to signify that the system is operating.

1. Dial in with the thumbwheel switches (optional matrix board, etc.) all of the information (numbers) that you desire to identify the type of analysis. For example, you have worked with the division systems programmer in designing three modes by which the computer assists in running the analysis. You select mode two via the thumbwheels, data such as sample size, its ID number, experimenter number, etc., parameters to be used in calculations can be entered, amount and rate of data to be sent, types of parameters to be controlled in the experiment, etc.

2. You can select either an automatic or manual mode of running the experiment. Select mode and the appropriate light illuminates.

3. Push the SET-UP button. It becomes illuminated.

4. Push SEND and the set-up words are transmitted with the SEND button becoming illuminated during the transmitting process. The SET-UP light turns off. The amber OPERATE becomes illuminated, signifying that the set-up words have been read and understood by the computer, and that it is now ready to assist you in running the experiment. If an error or invalid entry has been detected in the setup words, the computer will refuse to validate and a reject light is lit on the experiment panel.

5. When data are ready to be sent, push the DATA button (it illuminates); then push the SEND button and the automatic modes begins (or a single set of data are read in manual mode).

6. If you wish to terminate a run at any time, push the TERM button (it illuminates) and then the SEND button, and the computer will simulate a normal termination. If you wish to start over, push the covered ABORT button (it illuminates) and then the SEND button and the computer will destroy all of the data collected during the run.

7. You may change experimental conditions (sample number, experiment no., etc.) at any time, provided that this is allowed by your computer routine, by pushing RESETUP and repeating steps 1 through 5.

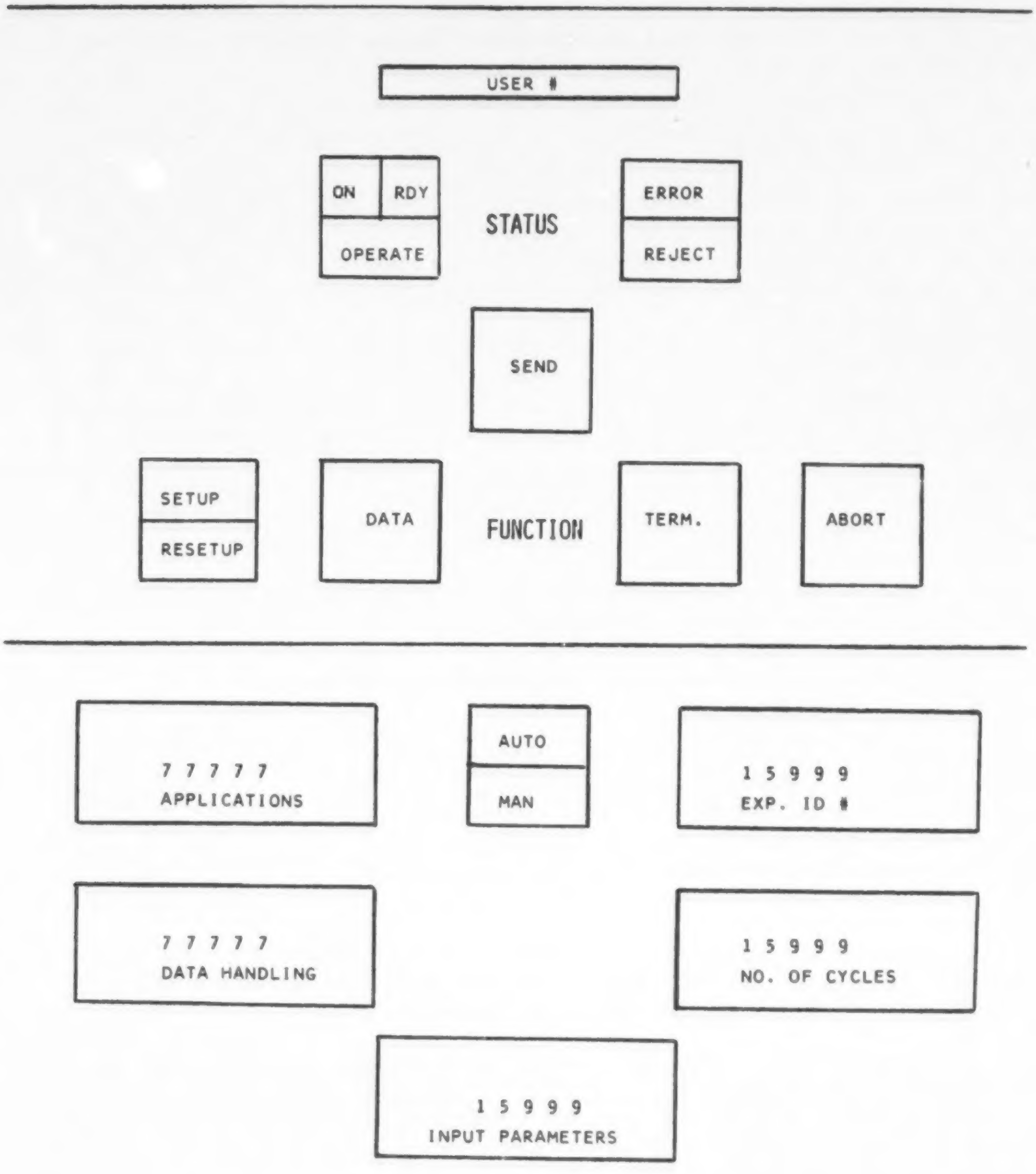

USER #
ON
RDY
OPERATE
STATUS
ERROR
REJECT
SEND
SETUP
RESETUP
DATA
FUNCTION
TERM.
ABORT
7 7 7 7 7
APPLICATIONS
AUTO
MAN
1 5 9 9 9
EXP. ID #
7 7 7 7 7
DATA HANDLING
1 5 9 9 9
NO. OF CYCLES
1 5 9 9 9
INPUT PARAMETERS

Figure 4. Operating panel of console.

8. If an experiment control signal was received from the computer in a garbled state (parity, etc.) an ERROR light will illuminate.

9. After the experiment terminated successfully, a short form of the results will be either placed on a teletype or graphic display in your laboratory.

10. All the lights except the ON light go out when the computer terminates the run.

CURRENT STATUS

At this writing the system is operational in a test configuration. This proves that it is operable, but its usefulness is determined only after experimenters are using the system. Plans are to bring one experiment on line per month over the next three years.

Changes in concept on computer systems design is extremely rapid because of advances in electronic components. It appears that in the next ten years most new equipment will have a small computer integral to it. Programming will be done on a very large remote-access computer which will generate code and load the small computers for running experiments. Maybe at this time the true research-assisting computer system will exist; but in the meantime, many man-hours of needless dial monitoring and bookkeeping can be eliminated by use of computer systems such as that described in this paper.

TRACE METALS IN SOILS

Olin C. Braids

Knowledge of the distribution and reactivity of trace metals in soils is necessary for an understanding of their role in ecology. Soil is a heterogeneous system - a mixture of inorganic particles of sand, silt, and clay interspersed with humified organic matter. The components range from surface inactive, sand, to highly surface reactive, clay and organic colloids. Because of differences in weathering, moisture regime, or organic matter content, soils may vary in color with location and depth. Only a few feet may separate one soil type from another. Color and texture may both differ between soil types.

I mention these points because I want you to realize that there is a large range of differences in soils. Thus, they are not all likely to fix, or release, or contain trace metals in similar quantity.

Included under the heading of trace metals are those which are essential for plant growth. They are: manganese, iron, boron, copper, zinc, and molybdenum, the micronutrients. Sulfur and chlorine are non-metallic micronutrients. Two characteristics the essential trace metals share are those of being required in rather low concentration (one pound of molybdenum added per acre will correct a deficiency of that element), and being toxic to plants in concentrations slightly exceeding optimal. It is the latter characteristic which many who are alarmed about pollution are concerned with.

Another suite of heavy metals can be considered under the topic of trace metals. These are transition metals which are not essential to plant growth, but which if present in soil solution may be taken up by plants. These also may be toxic to plants if present in great enough concentration. Included are nickel, cadmium, lead, chromium, selenium, and arsenic. Some soils naturally contain higher than average or even toxic quantities of one or more of these elements. However, these metals usually originate from external sources. Airborne particles carry lead from vehicular exhausts. Crop sprays may carry lead and arsenic. Sewage sludges applied to soils may carry nickel, cadmium, chromium, and other metals. Occurrence of toxic quantities of essential micronutrients or of the others is relatively rare. In fact, under ordinary conditions, a deficiency of trace metals is far more common than a surfeit.

In terms of geochemistry, only trace metals occurring in soil-forming minerals are of interest. During cooling of the magma, there was a differentiation of trace metals as they were included in the crystal lattice of igneous rock minerals. The ionic charge and radius of the metal dictated its ease of inclusion. The higher the charge and the smaller the ion, the greater the probability of inclusion. Electronegativity also influenced substitution as the less electronegative the ion, the greater the tendency to enter an ionic lattice.

As magmatic cooling progressed, magnesium, iron, cobalt and nickel became less concentrated in minerals because the first-formed minerals held most of the available ions. For example, the magnesium:manganese ratio in the first minerals formed is about 100; in the last of the series it is 1. Magnesium is small compared to manganese, so the magnesium became incorporated first and manganese (which has the largest radius in the group) was incorporated later. Zinc, copper, and molybdenum tend to be associated with sulfides. Copper, because of its high electronegativity, was partially excluded from silicates resulting in an inverse copper to silicon and direct copper to sulfur relationship.

In sedimentary deposits, copper, cobalt, zinc, molybdenum and boron are associated with fines. Iron and manganese distribution is more a function of the oxidation-reduction state of the environment during sedimentation than particle size. Boron, which is about uniform in igneous rocks, varies greatly in sedimentary rocks. A range of 5-10 ppm in igneous rocks is compared to 20-100 ppm in sedimentary rocks.

Table 1 shows concentrations of trace metals in igneous and sedimentary rocks, sewater, and soils. Order of magnitude estimates of plant uptake of these elements are also included. The solubility of boron is illustrated as it is the only element exceeding a 1 ppm concentration in sewater. Selenium is the least abundant element. Yet there are soils in the western United States which have selenium concentrations sufficient to induce selenosis in cattle browsing on plants growing there. Chromium has the widest concentration range. This is because some tropical soils are extremely rich in chromium. Cobalt is not listed as a required element for plant nutrition, but it is required for animal nutrition. There are areas, for example in Australia, where cobalt is so deficient that it must be supplemented in the animals' diet either directly or by soil application and plant uptake.

The weathering and distribution scheme for trace metals from primary mineals to soils is illustrated in *Figure 1*.

Each form is related to soil solution through a pseudo-equilibrium distribution which is a function of pH, oxidation potential, supply, and thermodynamic activity of the individual soil constituents.

Weathering releases the M^{++} ion into soil solution when it is free to react in a variety of ways. The equilibrium M^{++} MCh occurring in solution represents the soluble metal ion in equilibrium with its soluble metal-organic chelate.

Little explanation is needed of the first process, plant uptake. Ions which are in solution may be absorbed directly by plant roots and then translocated within the plant. I shall describe the remaining processes in more detail.

Table 1. Concentrations of trace metals in igneous and sedimentary rocks, seawater, and soils.

Trace Element	ppm concentration in a: igneous rocks b: sedimentary rocks c: seawater	Concentration in soils total ppm	Annual uptake by grasses and crops, kg
As	a: 2 b: 1-3 c: 3×10^{-3}	0.1-40	10^7
B	a: 10 b: 20-100 c: 4.6	2-100	10^8
Cd	a: 0.2 b: 0.03-3 c: 1.1×10^{-4}	0.01-7	10^7
Cr	a: 100 b: 10-100 c: 5×10^{-5}	5-3000	10^7
Co	a: 25 b: 1-20 c: 2.7×10^{-4}	1-40	10^6
Cu	a: 55 b: 5-45 c: 3×10^{-3}	2-100	10^8
Pb	a: 12.5 b: 5-20 c: 3×10^{-5}	2-200	10^7
Ni	a: 75 b: 2-70 c: 5.4×10^{-3}	10-1000	10^7
Se	a: 0.05 b: 0.1-1.0 c: 9×10^{-5}	0.1-2.0	10^7
Zn	a: 70 b: 10-100 c: 0.01	10-300	10^9

(from Allaway)

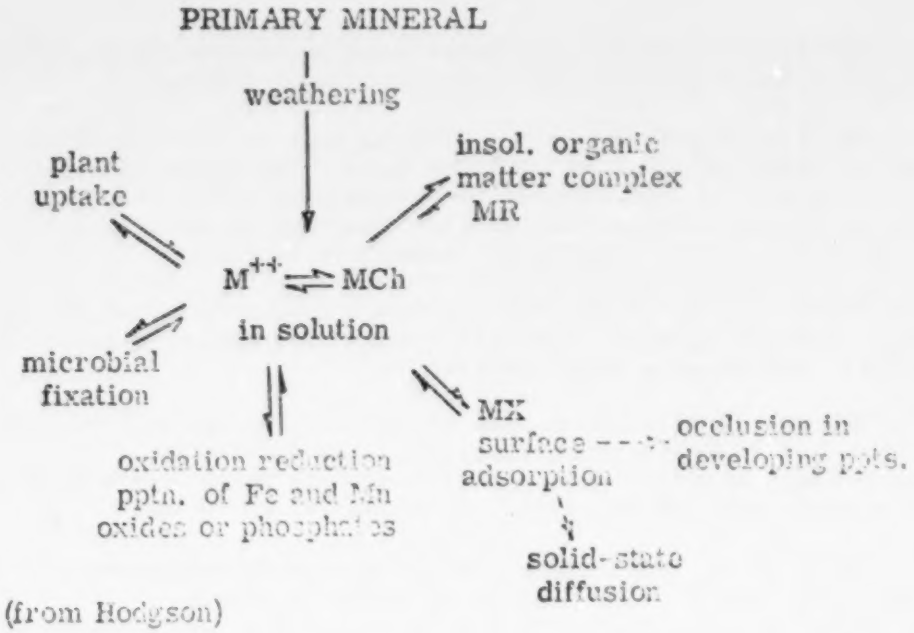

PRIMARY MINERAL
weathering
plant uptake
insol. organic matter complex MR
M^{++} ⇌ MCh in solution
microbial fixation
oxidation reduction pptn. of Fe and Mn oxides or phosphates
MX surface adsorption
occlusion in developing ppts.
solid-state diffusion
(from Hodgson)

Figure 1. The weathering and distribution scheme for trace metals from primary minerals to soils.

Microbial processes

Microbial processes influence micronutrients in at least five ways:

1) Release of inorganic ions during decomposition of organic materials.

2) Immobilization of ions by incorporation into microbial tissue.

3) Oxidation of an element such as iron or manganese into a less available form.

4) Reduction of the oxidized form of an element in an oxygen deficient environment.

5) Indirect transformations of micronutrients resulting from pH or oxidation potential changes.

The first two points can be grouped because decomposition of plant residues is effected by soil micro-organisms. As they release trace metals from plant tissue, they also immobilize some in their own tissue. After the major part of the energy-producing material in plant residue is used up, the microbial population wanes and lysis of the cells again returns micronutrients to the inorganic side of the cycle.

The most significant effect microbes have on trace metal status is that of their influence on the redox state. The oxidation state of manganese in soil is controlled by micro-organisms. That soil micro-organisms could oxidize manganese was first observed in 1913. Manganese in its oxidized form is essentially unavailable to plants. An illustration is the gray speck disease in oats. It is caused by a manganese deficiency which in ordinary soil results from a concentration of 14 ppm or less. However, in sterilized soil a manganese level of 5 ppm is sufficient to prevent gray speck symptoms.

The role of microbes in iron oxidation is not as well defined because iron undergoes chemical oxidation in sterile soil. It has been demonstrated in soil columns that a ferrous to ferric reaction followed the sigmoid curve characteristic of biological processes.

Reduction of both metals is an energy-requiring process. It proceeds especially rapidly when an easily decomposable organic substrate is present in a system of low oxidation potential. Thus, micro-organisms are shown to be very important in carrying out reductive reactions.

Oxidation-reduction state

There is no evidence that cobalt and molybdenum are effected by the redox state of the soil. Under conditions of poor drainage, soil becomes oxygen deficient and its oxidation potential is reduced. Visibly this is manifested by gray, mottled subsoil. Under reduced conditions, cobalt uptake by plants and its extractability with acid dithizone was enhanced. Copper also reacts in a similar fashion.

These phenomena are thought to result from the effect on metal ion solubility of complexation with organic decomposition products rather than a change in oxidation state of the metal. Organic compounds produced anaerobically are more effective solubilizers of heavy metals than corresponding aerobic products. Certainly more data are necessary before a quantitative prediction can be made about aerobic vs. anaerobic availability of trace metals.

Surface adsorption

Clay minerals occurring in soils carry a net negative charge resulting from broken bonds at lattice edges, isomorphous substitution within the lattice, and iron and aluminum sequioxides which may coat the surface. The crystal lattice is made up of silicon tetrahedra and aluminum octahedra. Silicon is coordinated with four oxygen atoms and aluminum with six oxygen atoms. A small amount of aluminum can substitute for silicon. Large amounts of iron and magnesium may substitute for aluminum. In each case a negative valence is left unsatisfied. Tetrahedral and octahedral layers share oxygen atoms to form sheets. The sheets are joined by each apical oxygen of the tetrahedral sheet, replacing one hydroxyl position of the oxtahedral sheet. The sheets stack to form clay particles whose surfaces attract cations.

Kaolinitic clays are composed of 1:1 tetrahedral:octahedral layers. Illitic and montmorillonitic clays have a 2:1 tetrahedral:octahedral layer ratio. Montmorillonitic clays have expanding crystal lattice structures. Water is adsorbed between the crystal layers opening up the lattice. This allows cations to become adsorbed along the inner surfaces. This process substantially increases the reactive surface of montmorillonite. The differences in crystal lattice structure is reflected in the following table of cation exchange capacities.

Mineral	Cation exchange capacity (meg/100g)
Kaolinite	3-15
Illite	10-40
Montmorillonite	80-150

The adsorptive strength of trace metal ions is dependent upon several factors. Zinc, copper, ferric ion, or thorium, which form weak bases, are held strongly. This may result from formation of basic salts with clays in which only a part of the valency goes to the exchange complex. Most of the biologically-active cations are readily adsorbed by active clay minerals and are difficult to displace. The order of difficulty is approximately: Cu > Pb > Ni > Co > Zn > Ba > Sr > Ca > Mg > Na > Li. Relative positions may vary with concentrations of reactant and the nature of the exchange-active mineral.

Organic matter complexes

Organic matter is the most reactive fraction of soil on a unit weight basis. We will first discuss water-insoluble organic matter, which comprises the bulk of organic matter in soil. It includes partially decomposed plant and/or animal residues which are resistant to further decomposition. These humic materials are highly polymerized and include humic and fulvic acids, polysaccharides, hemicelluloses, and chitins.

Humic material in soil has a cation exchange capacity of as much as 300 meg/100g. Several functional groups are active in complexing and chelating trace metal ions. These include carboxylic acid, phenolic hydroxyl, amino, organic phosphate, and porphyrin. Some of these structures are illustrated in *Figure 2*. The trace metals we have discussed are members of the inner transition series of the periodic table and thus have the ability to form coordination complexes with organic ligands.

The stability of organo-metallic complexes is illustrated in muck soils which consist of 95-98 percent organic matter. Several micronutrient deficiencies may occur in these soils as a result of complexation.

Table 2. **Metals contained in Chicago sewage sludges**

Tenny & Stanley, (1967)

	Calumet % dry wt	lbs/day	Stickney % dry wt	lbs/day
Cu	0.118	184	0.205	3309
Cr	0.168	262	0.360	5810
Fe	6.060	9454	2.930	7920
Zn	0.334	521	0.651	10507
Ni	0.001	0.2	0.045	726
Cd	0.007	11	0.047	759
Mn	0.052	81	0.020	323
Pb	0.327	510	0.085	1372

Table 3. Micronutrient content of fertilizer materials.

Micro-nutrient	ppm in rock phosphate	ppm in super-phosphate	ppm in potassium salts
B	10-50	0-20	0-500
Cu	1-50	10-100	0-10
Co	1-10	1-10	<1
Ni	1-10	1-10	1-10
Pb	1-10	5-100	<1
Mo	1-20	1-20	<1
Zn	50-1000	50-1000	0-10
Mn	10-1000	10-1000	0-10
V	10-1000	50-2000	<1
Cr	100-500	10-500	1-10
Ti	10-1000	10-1000	<1

Deficiency symptoms in plants have been observed for manganese, zinc, copper, and iron.

On the other hand, addition of organic residues (crop residues or animal manure) to mineral soils often enhances uptake of micronutrients. This is due to formation of products which in turn form soluble complexes or chelates with the metals. In this way, the metals are protected from precipitation with anions or adsorption on clay surfaces. Such soluble organo-metallic compounds are thought to be implicated in the podzolization process. A podzolic soil is characterized by an iron and organic matter-poor bleached gray horizon near the surface. It is underlain by an iron and organic matter-rich horizon. Organic compounds released from decomposing forest litter as they are leached into the soil apparently complex with and solubilize iron carrying it from one zone to a lower, where it precipitates and is deposited.

We have covered most of the factors affecting availability in our discussion of organic matter influence, the influence of the redox condition of soil, and the influence of microbial reactions. One remaining factor, pH, should be discussed briefly.

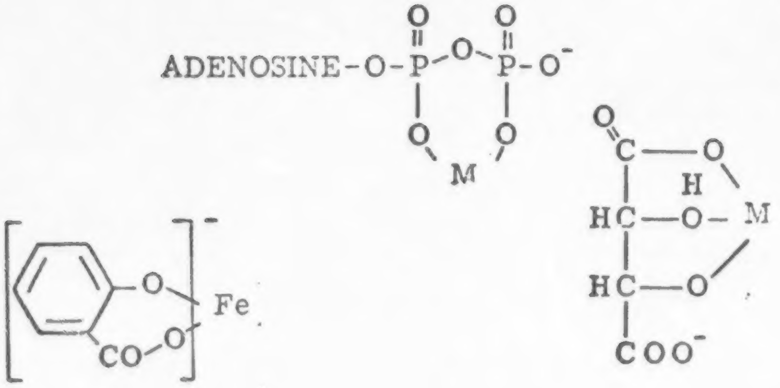
Microbial activity, absorptivity of plant roots, ionic transport within plant roots, stability of soluble and insoluble organic complexes, solubility of antagonistic ions, and alteration of the rhizosphere (microbial population contiguous to plant roots) are affected by soil pH. In the pH range 5-8, manganese, iron, cobalt, zinc, copper, and boron are more available at the lower than at the higher extreme. Molybdenum availability is just the opposite.

External Sources

There are many sources of trace metals external to soil which contribute trace metals to soils. Some supply a particular metal, while others may supply several simultaneously. A familiar source is vehicular exhaust which disperses lead halides in particulate form. Small amounts of lead are brought to earth in precipitation as a result of nuclear decay of radon to lead in the atmosphere. Cadmium and zinc are carried in abraded particles of vehicle-tire rubber. Animal manures contain zinc, copper, manganese, and boron in significant quantities. Sewage sludges from municipal treatment plants generally contain zinc, copper, manganese, iron, and lead. Depending upon the industrial effluents which are discharged to the treatment plant, such metals as cadmium, chromium, nickel and mercury may be present.

Figure 3 indicates how organic wastes are cycled in soil. The mineralization step releases trace metals as well as the sulfate and phosphate ions.

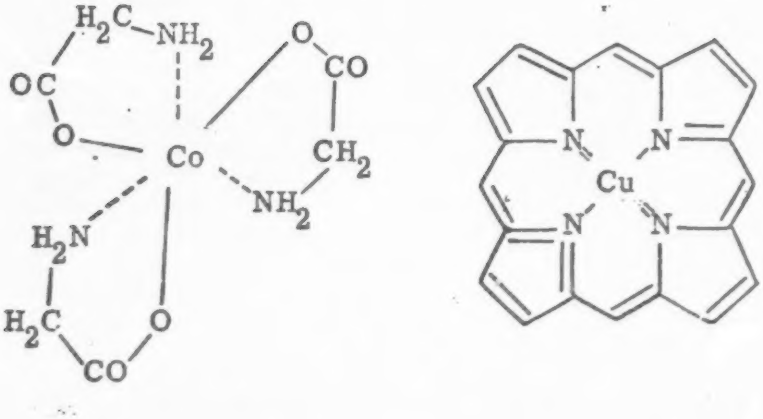
As an example of an external source of trace metals, some data are listed for sewage sludges from treatment plants of the Metropolitan Sanitary District of Greater Chicago. *Table 2* shows the content of metal in percent dry weight and in terms of the number of pounds per day of the metal entering the treatment plant.



Fe (III) Salicylate
Phenolic

Phosphate

Tartrate
Organic Acid



Trisglycinocobalt (III)
Amino Acid

Porphino-Cu (II)
Metallo-Porphyrins

Figure 2. Some possible structures for organo-metallic compounds occurring in soil.

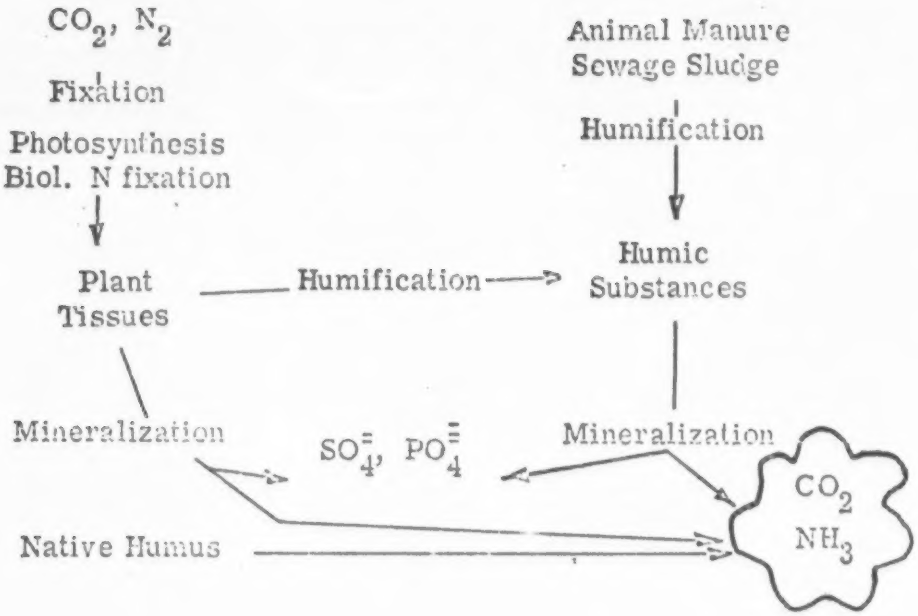

CO_2, N_2
Fixation
Photosynthesis
Biol. N fixation
Plant Tissues
Humification
Animal Manure
Sewage Sludge
Humification
Humic Substances
Mineralization
$SO_4^=$, $PO_4^{\equiv}$
Mineralization
CO_2
NH_3
Native Humus

Figure 3. Organic residue cycling in soil.

Commercial inorganic fertilizers are also carriers of trace metals. High analysis types which have been developed and become popular in recent years are relatively free, but fertilizers derived from rock phosphate may carry significant quantities of trace metals. Table 3 lists a few of the micronutrients and their concentration ranges in fertilizers.

In areas where warranted, high analysis fertilizers are formulated with micronutrients to provide a convenient source for the production of healthy crops.

The title "Trace Metals in Soils" may have conjured up visions of mercury, cadmium, or copper poisoning. I hope you were relieved to hear that the greatest agronomic problem is with deficiencies, not toxicities. However, in order to understand either, with the goal of control, one must be aware of the factors which we have just briefly discussed.

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TRACE ELEMENTS AND PLANT GROWTH

R. J. Miller and D. E. Koeppe

Introduction

All living organisms obtain their supply of essential elements from a thin layer of matter on or above the crust of the earth. Until recent years these essential elements cycled naturally in the environment. But, as man has evolved he has developed technology to alter the slow, natural processes. Man's use of this technology has brought about a redistribution of elements so that presently living organisms are being exposed to increasing amounts of elements that were either not present in their environment before, or are now present in concentrations which the organism cannot tolerate. These latter elements and their effects on higher plants will be discussed in this paper.

Man is ultimately concerned with trace elements only if they have an adverse effect on man himself, or if they affect some process or organism upon which man is dependent. The two ways that man can acquire trace elements is by ingestion and by respiration; through the food chain or through the air. In many cases the knowledge to reduce or prevent trace elements in the air is at hand, but whether there are the social and economic incentives to remove these pollutants is another question. The most serious long-term way that man may be exposed to trace elements is through the food chain. Water and aquatic life are parts of this food chain which will be dealt with in subsequent papers. We are concerned with the terrestrial food chain. The cycling of trace elements is depicted in *Figure 1*. This chain is basically the incorporation of sixteen essential elements into plant matter which then may be consumed by animals. Man may ingest the plants directly, or may secondarily consume other animals which have fed on plants. Because of the important role of plants in nutrient and energy cycling, we wish to direct ourselves to the question of how trace elements affect plants.

Plant Nutrients

Plants obtain the majority of their nutrients from the soil. Because soils are derived from so many sources, most elements are present in some amount in most soils. But the presence of the element in the soil does not mean that it is available to the plant. *Table I* lists the concentration of some elements in the soil as well as the concentration in the soil solution. The concentration of the element in the soil solution is more representative of that available to the plants than is the total concentration in the soil. A mor realistic plant availability term is ionic activity, which is a measure of the ability of the ion to participate in chemical or biological reactions, one of which is uptake by the

TRACE ELEMENT CYCLING:

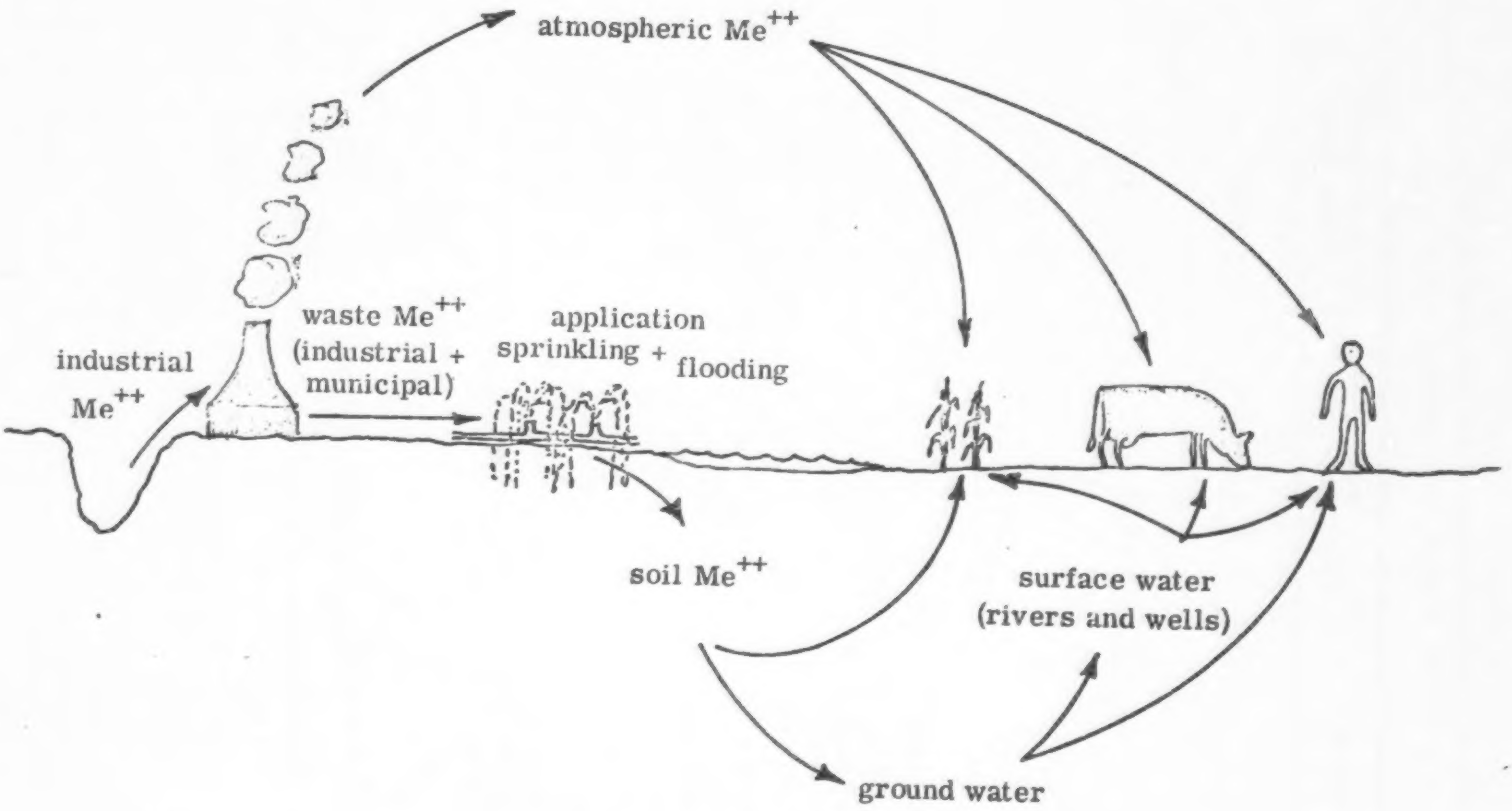
atmospheric Me++
industrial Me++
waste Me++ (industrial + municipal)
application sprinkling + flooding
soil Me++
surface water (rivers and wells)
ground water

Figure 1. A schematic diagram of trace element cycling. (Trace element indicated by Me^{++}.)

Table I. Composition of soils and soil solution for some of the elements.

element	Soil ppm (average)	Soil Solution ppm (range)
arsenic	6	-
boron	10	0.03 - 10
beryllium	6	-
carbon	20,000	2 - 7 (HCO_3^-)
calcium	13,700	1 - 60
cadmium	0.06	-
chlorine	100	7 - 50
cobalt	8	-
chromium	100	-
copper	20	0.01 - 0.06
iron	38,000	0.1 - 0.25
mercury	0.03	-
potassium	14,000	1 - 11
magnesium	5,000	0.7 - 100
manganese	850	0.02 - 2
molybdenum	2	<0.001
nitrogen	1,000	2 - 800 (NO_3^-)
nickel	40	-
phosphorous	650	0.001 - 30
lead	10	-
sulphur	700	<3 - 5000
tin	10	-
zinc	50	0.1 - 0.3

Table II. Essential elements for the growth of most plants.

Macronutrients	Micronutrients
carbon	chlorine
hydrogen	iron
oxygen	manganese
nitrogen	boron
phosphorus	zinc
calcium	copper
sulphur	molybdenum
potassium	
magnesium	

plant. Unfortunately, activities are seldom available, but are needed if we are to understand ion-plant interactions. *Table I* shows that there is not necessarily any relationship between total analysis and the amount present in soil solution; it also shows that our knowledge about some elements in the soil is lacking.

Of the elements found in the soil and atmosphere, sixteen are generally considered to be essential for plant growth. These sixteen are listed in *Table II* and are divided into the macronutrients and the micronutrients. These divisions are arbitrary, but in general the macronutrients are needed in greater quantity. While these elements are essential for plant growth, if they are present in large enough quantities they can be toxic. The available concentration of these elements in soil varies all the way from insufficient to toxic (*Fig. 2)*.

A trace element is an element that is present in small quantities. Some of the trace elements with a potential affect on plant growth are listed in *Table III*. If we compare *Tables II* and *III* it is seen that three of the essential plant elements are considered to be potentially noxious trace elements; these are: copper (Cu), manganese (Mn), and zinc (Zn). To date none of the other elements listed in Table III have been shown to be necessary for plant growth. Since Zn, Cu and Mn are essential for plant growth, a good deal more is known about their roles in plants than the other trace elements.

The affects of non-essential trace elements on plant growth will likely depend on their concentration in the plant, as depicted in Fig. 3. There are two means of plant exposure to trace elements: air and soil. For example, aerosol forms are a major source of lead--particularly within short distances of roads. Industrial and municipal organic wastes contain relatively large amounts of all previously-mentioned trace elements (Cr, Cd, Hg, Pb, Ni). If the disposal of these wastes on agricultural land becomes a common practice as predicted by some, then plants growing in areas of such disposal would be exposed to these trace elements. Since little is known about trace element activity and availability to plants, and since land disposal of organic wastes is a realistic way of re-introducing many materials back into their biogeochemical cycles, trace element problems could arise in soils used for this purpose.

The effects of copper, manganese and zinc are presented in many excellent reviews (1, 2 and 3) and will not be discussed here. Although nickel is not essential for plant growth, it is found in most plants and occurs in some soils in potentially deleterious quantities. As a result, the effects of nickel on plant growth have been extensively studied. A summary of these effects can be found in the above references.

To our knowledge there are no reports of the effects of chromium or mercury on plant growth. But it is not unreasonable to expect that they would affect plant biochemical processes in many of the ways they influence these processes in mammals. On such effect is the poisoning or inactivating of enzymes, while another is on cell membranes and therefore on transport processes *(1)*.

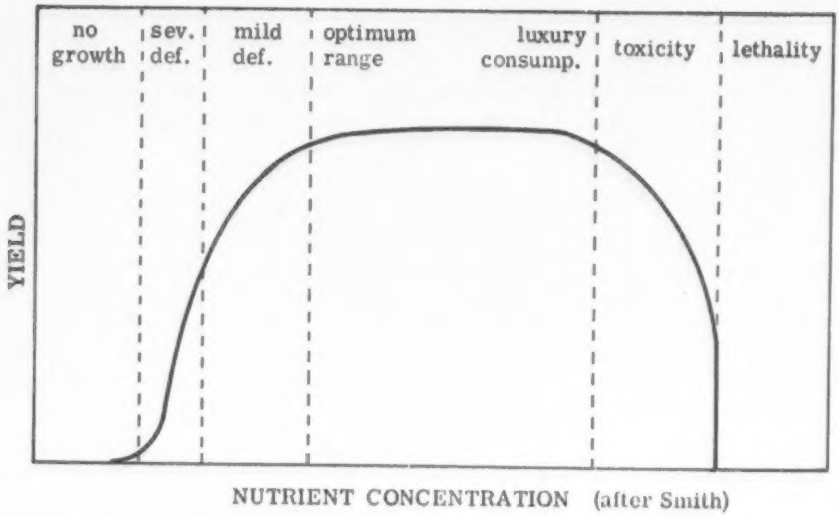

Figure 2. General effects of the concentration of an element on the growth of plants. (After P. F. Smith, *Ann. Rev. Plant Physiol.* 13:81. (1962)

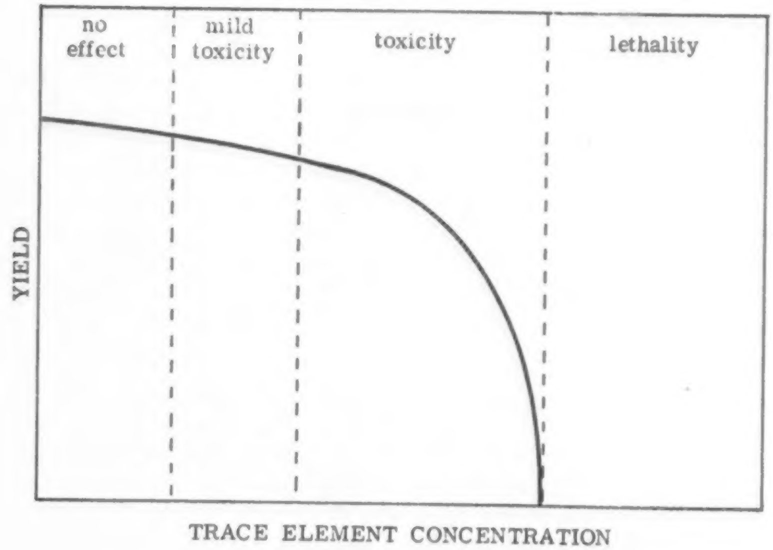

Figure 3. General effects of a non-essential trace element on plant growth.

Table III. Trace elements potentially harmful to plants.

copper
manganese
zinc
nickel
chromium
mercury
cadmium
lead

Table IV. Lead and phosphate concentrations in the lower leaves of 22-day old corn plants.

	With Phosphate		Without Phosphate	
Pb added µmoles	Pb (µg/gm dry wt)	(µg/gm dry wt)	Pb (µg/gm dry wt)	P (µg/gm dry wt)
Check	trace	6099 ± 47	trace	1950 ± 23
60	"	5355 ± 724	264 ± 17	1589 ± 288
600	126 ± 6	4611 ± 539	479 ± 47	1333 ± 234
4000	1700 ± 654	3800 ± 75	11,639 ± 1000	2117 ± 118
6000	2029 ± 437	4050 ± 71	10,083 ± 622	2217 ± 494

Note: The plants were watered with complete Hoagland's nutrient solution or Hoagland's solution without phosphate, and were treated with 0, 60, 600, 4000, or 6000 µmoles of $Pb(NO_3)_2$ as indicated in the text. Standard deviations are reported with each result.

Lead (Pb)

The interest in lead has primarily arisen because of the aerosol deposition of lead, from automobile combustion, near roadways. The accumulation of lead in soils and plants near roadways has been well documented *(4, 5, 6, 7, 8, 9)*. Lead concentrations as high as 700 ppm have been found in soils *(8)* and as high as 3,000 ppm in grass *(4)*. Since most of the lead associated with roadside plants can be removed by washing, aerosol lead is the suspected source of most of the lead in the aerial tissues of these plants *(5, 6, 7, 9)*. Until recently there has been little evidence that lead could be translocated from roots to shoots *(7, 10, 11)*, but these experiments were conducted using soils with a relatively high organic matter and clay content. In soils where the total lead content was high, no data on the activity of lead were presented. It is possible that under the above conditions the lead was not available to the plant even though present in the soil. If plants do not internally incorporate lead, and if, in the future, the major exposure of plants to lead will only be under roadside conditions or those treated with organic wastes, then why worry about lead in food chains?

Miller and Koeppe *(12)* working with corn plants grown in sand culture in the greenhouse have shown that plants take up large amounts of lead from sand, that lead can be toxic to corn plants, and that there is a lead-phosphate interaction. In these experiments corn was grown in sand with and without phosphate in the nutrient media. On the sixteenth day after initial watering of the seed, lead treatments were begun on all plants and made each day for 6 days. Total lead applications were 0, 60, 600, 4000, or 6000 μmoles of lead nitrate. On the 22nd day after initial watering the plants were harvested and subsequently analyzed for lead by the dithizone method *(13)*.

Figures 4 and *5* show that lead does affect the growth of corn plants. Sixty μmoles of Pb had no effect on the phosphate-sufficient (+P) plants, while under phosphate-deficient conditions (-P) 60 μmoles of Pb retarded growth. The 600 μmole Pb treatment retarded the growth of P deficient plants. The lead was without effect on plants grown with sufficient phosphate, although phosphate deficiency symptoms were observed. Lead at 6,000 μmoles killed the -P plants and caused pronounced P deficient symptons and decreased growth in the +P treated plants.

Corn leaves accumulated large amounts of lead in response to the quantity of lead applied and the phosphate status of the plant (*Table IV*). The +P plants did not accumulate measurable lead when treated with 60 μmoles of Pb, but did at all higher Pb treatments. The -P plants accumulated lead at all treatment levels, and in much larger quantities than the +P plants.

The phosphate concentration in the plants grown with phosphate depended on the amount of lead applied up to the 600 μmole level, but was without change above it. The phosphate content of the -P plants was very low, but constant as expected. Even at the 6,000 μmole level the +P plants

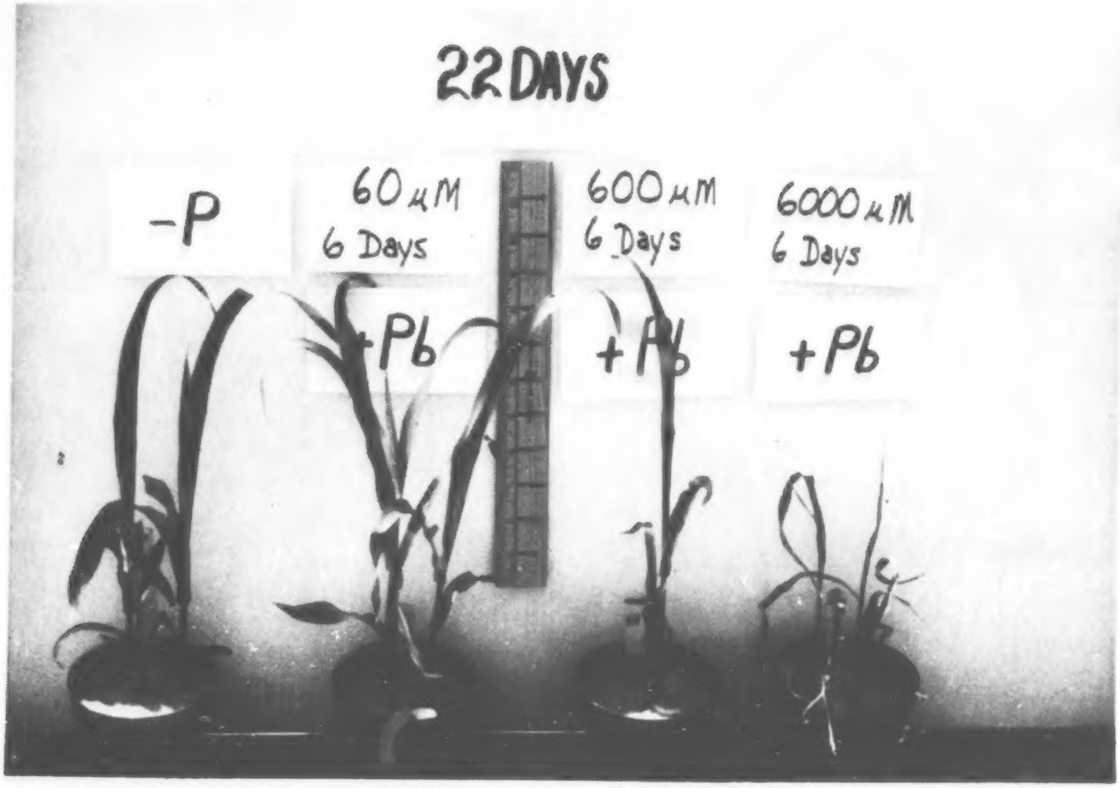
22 DAYS
-P
60 µM
6 Days
+Pb
600 µM
6 Days
+Pb
6000 µM
6 Days
+Pb

Figure 4. The effects of 60, 600, and 6,000 µmoles of $Pb(NO_3)_2$ on the growth of corn plants watered with Hoagland's nutrient solution without phosphate. Lead was applied for the last six days of growth.

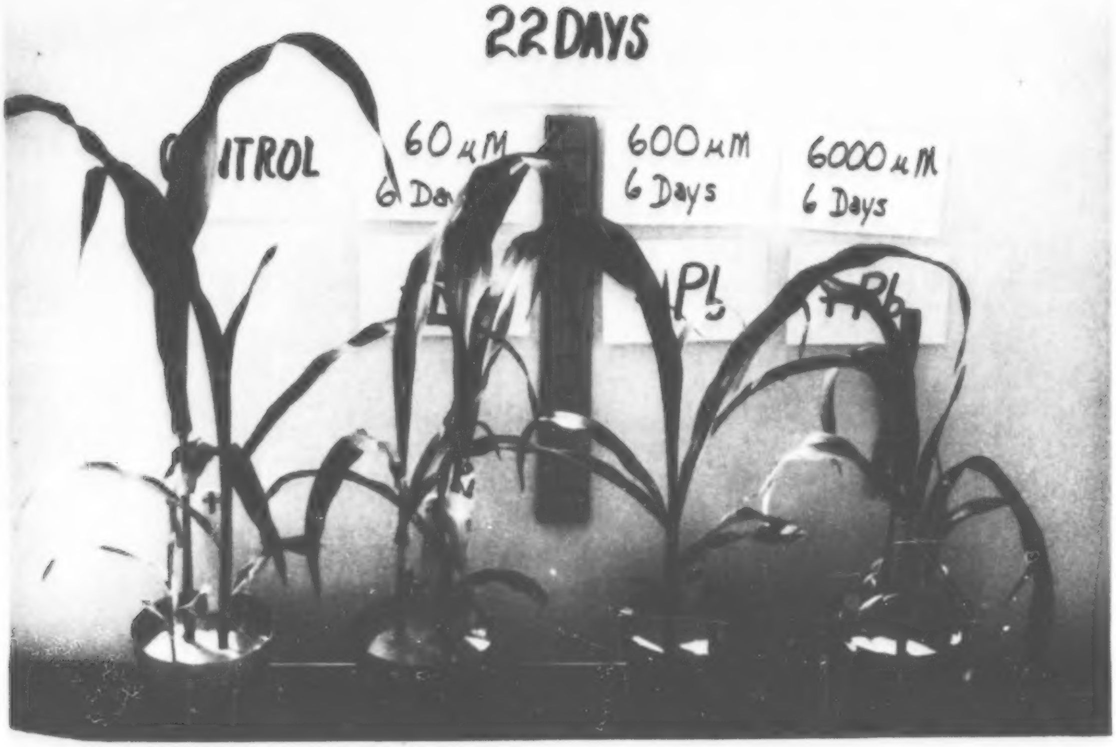
22 DAYS
CONTROL
60 μM
6 Days
600 μM
6 Days
Pb
6000 μM
6 Days
Pb

Figure 5. The effects of 60, 600, and 6,000 μmoles of $Pb(NO_3)_2$ on the growth of corn plants watered with complete Hoagland's nutrient solution. Lead was applied for the last six days of growth.

contained a sufficient concentration of phosphate for normal growth, yet they exhibited phosphate-deficient symptons. This indicates that either the lead is making the phosphate unavailable for the physiological processes of the plant even though present, or lead toxicity produces the same symptoms as phosphate deficiency.

The addition of 60, 600, and 6,000 µmoles of lead nitrate to the sand corresponded to applied concentrations of approximately 24, 240, and 2,400 ppm. These concentrations of Pb are not too different from some levels of lead found in roadside soils, although the form of the lead is likely different. It should be realized that in the +P systems not all of the applied lead was available to the plant, since over the same 6 days that the lead was applied 1350 equivalents of phosphate were also applied. Since lead phosphate is quite insoluble, this amount of applied phosphate was sufficient to potentially precipitate all of the lead in the 60, and 600 µmole treatment and about 10% of that in the 6000 µmole treatment. This means that both the +P and -P plants at the 6000 µmole treatment level had about equal amounts of lead available, yet the -P plants took up considerably more lead.

These studies show that corn can translocate and accumulate large amounts of lead and that lead can be concentrated by this step in the food chain. They also show that the accumulation of lead is not simply related to soluble lead in the growth media, but must also depend on the physiological and nutrient status of the plant. This suggests that adverse lead affects are more likely to be observed on phosphate deficient soils.

If lead does accumulate in plants to a toxic level, what are the physiological effects of such an accumulation? Because the number of enzymatic reactions is huge, little is known about the effects of lead on any of these specific reactions. Other work from our laboratory indicates that mitochondria, energy-converting organelles found in the cytoplasm of both plants and animal cells, are sensitive to cations in general. Since mitochondria isolated from plants (*in vitro)* have the ability to oxidize several substrates (fuels), the effects of lead on these oxidative reactions was determined. *Figure 6* shows that lead had a pronounced effect on the oxidation of two of these substrates, succinate and NADH, and no effect on the oxidation of the third, malate. It is of further interest to note that lead stimulated the oxidation of NADH, but inhibited the oxidation of succinate. The presence or absence of phosphate was also important. This work may delineate one of the primary sites of the action of lead and suggests that if free lead is present in the cytoplasm it may at one site inhibit metabolism, while at another cause the rapid consumption of energy sources,--the total effect being a reduction of the energy supply for plant growth.

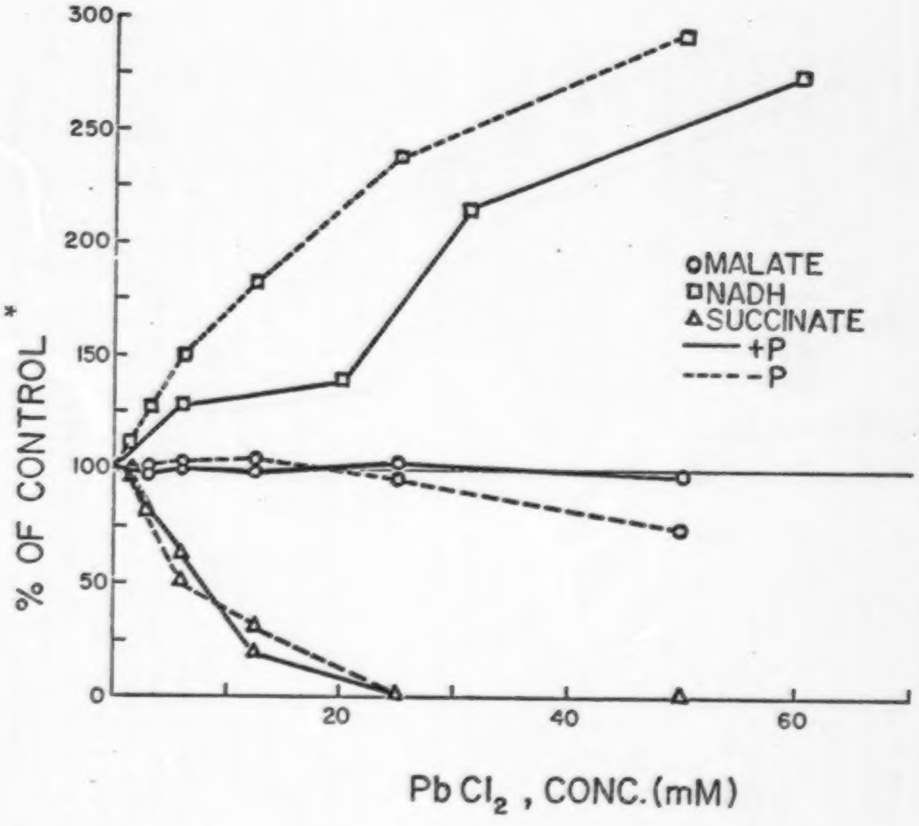

Figure 6. The effect of $PbCl_2$ on the respiration of NADH, malate, and succinate by isolated corn shoot mitochondria.

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* The percent of control was determined by taking the rate of O_2 uptake from the reaction media without lead and calculating the change in O_2 uptake as a function of lead content. Reaction conditions were as described by Miller and Koeppe *(12)*.

Cadmium

The effects of cadmium on plant growth are virtually unknown, but it is known to be very toxic to man and is found in relatively large quantities in the organic wastes from municipal-industrial sewage plants. This presence could pose certain problems in the future.

Since *in vitro* mitochondria may predict what the effects of lead on plants might be, studies were conducted to determine the effects of cadmium on the respiration of corn mitochondria. Cadmium inhibited the oxidation of succinate and malate at all concentrations tested, but at low concentrations stimulated the oxidation of NADH *(Figure 7)*. Further studies indicated that cadmium stopped the ability of the mitochondria to produce ATP, the usable energy source needed for almost all growth processes. On the basis of these data it might be that cadmium could be toxic to plants if physiologically available.

CONCLUSION

Other than the trace metals essential for plant growth, little is known about how other trace elements affect plant growth. Of the elements Ni, Pb, Hg, Cd, and Cr, there is some information on the effects of Ni on plant growth, and in recent years some of the effects of Pb have been studied. Little is known about the effects of Hg, Cd, or Cr.

Data have been presented that show that lead can be accumulated in the leaves of plants after translocation from the roots. Similar studies indicate that lead is toxic. But the effects of lead on the plant depend on the amount of lead and the physiological status of phosphate within the plant.

Data have been presented which show that both Pb and Cd affect plant mitochondrial processes. Thus, both are capable of altering energetic processes within the plant.

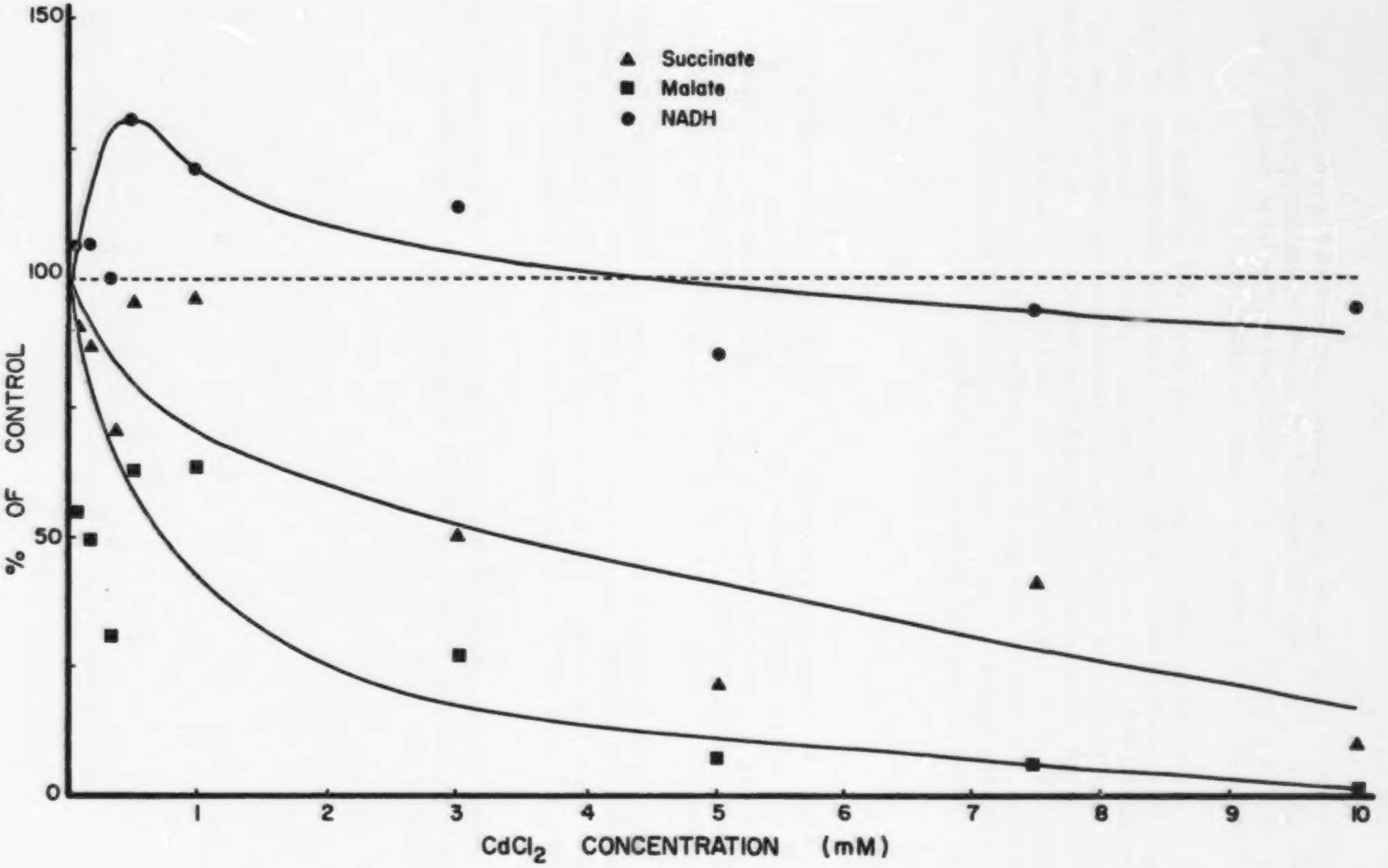

Figure 7. The effects of cadmium chloride on the rate of reduction of 2, 6 - diphenolindolephenol (DPIP).

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TRACE METALS IN COAL

H. J. Gluskoter

Introduction

Although this discussion was originally entitled "Trace Metals in Fossil Fuels," I am actually going to restrict myself to a discussion of coal. The reason for doing so is that I know even less about oil and gas than I do about coal; but I can also justify doing so for other reasons equally as practical. First, gas is extremely clean--relative to oil and coal--and, second, oil as it occurs in the ground and the petroleum products consumed have little resemblance to each other. The complex chemical treatment and the addition of various additives (some highly touted in radio and television commercials) may radically alter the trace metal composition of the petroleum products, whereas the trace metal constituents of coal are not greatly affected by the physical methods sometimes used in cleaning coal.

Composition of Coal

Coal is defined in a variety of ways, but, "a readily combustible rock containing more than 50 percent carbonaceous material (by weight) formed from compaction and induration of variously altered plant materials," hits the high spots. Coal's precursor is peat; the lowest rank coal is called lignite, which is more than 33 percent water by weight and 65-75 percent carbon (when calculated to a dry basis). An increase in rank produces bituminous coals and then anthracite, which contains more than 92 percent carbon in a dry basis.

Coals in Illinois formed during the Pennsylvania Period of the Paleozoic Era approximately 280 to 325 million years ago. Other rather extensive coals in North America formed during the Triassic and Cretaceous Periods 100 to 200 million years ago, and still others formed during the Cenozoic, just tens of millions of years ago. Peat, which is forming today, could eventually become coal.

Coal is made up of the remains of plants growing in a peat swamp at some point in time. Not all swamps in the world are just alike at any one time, and, because of the evolutionary changes in flora, there are emportant differences in peats that have been formed at different geologic times. Although coal is defined as being organic, a small amount of inorganic material is associated with it. The term "mineral matter" has been applied to all inorganic noncoal material occurring in coal and also to those elements usually considered to be inorganic, even if they are in organic combination. That is, all elements in coal except carbon, hydrogen, oxygen, nitrogen, and sulfur are automatically considered to be a part of the mineral matter, and four of these "organic" elements even occur in coals in inorganic combination. Carbon may be present in carbonates [$Ca(Fe,Mg)CO_3$]; hydrogen in free water and water of hydration; oxygen in water, oxides, carbonates, sulfates, and silicates; and sulfur in sulfides (primarily FeS_2) and sulfates.

The mineral matter may compose as little as a few percent of the total coal. But, at the other end of the scale is an inorganic sedimentary rock with a small amount of organic matter in it. We generally stop using the term "coal" for this continuum when the inorganic fraction makes up more than 50 percent (by weight--including inherent moisture) of the sample.

Origin of Trace Metals in Coal

We are interested in what trace metals are present in this mixture I have defined and with what part of the coal it is associated, and when and how it got there. However, we should be prepared to find large variations in chemical composition in a substance as varied as coal.

1. The original plant material that grew in the swamp--that existed before the coal--took up trace elements during its life by physicochemical processes. Some of these were necessary to sustain plant life. Plant species vary freatly in the amount of trace minerals they take up, and correlating the plants of a coal swamp that existed 300 million years ago with modern vegetation is beset with obvious difficulties. The trace metals in the living plant are not necessarily preserved in the coal, for the plants have partially decayed and the peat has been metamorphosed into coal. There may have been appreciable amounts of these trace metals either added to the system or subtracted from it. The geochemical system with which we are dealing is a relatively low-temperature, low-pressure system with a large number of component phases. It is an open system, and many of the components are mobile. We also have the further complication that the system has been active and may have been in the process of altering at any time during its approximately 300 million years (for coals of the Pennsylvanian Period) of existence.

2. Within the peat swamp, minerals were deposited concurrently with the plant material. These were exposed to the same environment as the plants, but certainly responded differently to it. They, too, may have been altered with respect to trace metal composition since they were deposited. This is especially easy to picture in the case of the clay minerals with their large capacity for ion-exchange.

Another group of minerals was deposited within the coal bed following the time of the coal swamp. Kaolinite, calcite, pyrite, and gypsum commonly occur along vertical fractures in the coal bed. The trace metal composition of these will depend on the geochemical conditions of their formation and also on their response to the environments that followed.

The major minerals in coals of the Illinois Basin are: clay minerals (kaolinite, illite, and mixed-layer illite-montmorillonite), pyrite (FeS_2), calcite ($CaCO_3$), and quartz (SiO_2). Various other minerals have been reported as occurring in coal at some time, from some place, by some worker.

Analyses of Coal

A wide variety of chemical analytical techniques has been applied to coal and to the determination of trace metals in coal ash. As more modern techniques are developed, they too will certainly be applied. We are now concerned with the occurrence of trace metals in coal because of their possible deleterious effects on the environment. Therefore, we are most interested in those heavy metals that are emitted into the atmosphere when the coal is burned. Almost all of the work done to date on the trace metal content of coals has been done on coal ash, and we cannot be certain that the volatile elements are retained in the ash.

While we are confident that a number of elements are entirely retained in the ash (Si, Al, Fe, Ca, K, Na), we are also aware that a large portion of some elements are lost during ashing (S, P). In the case of most of the trace metals, no work has been done to demonstrate either the retention or loss of the element during ashing. Until such work is done, we can only view the results of trace metal analyses of coal ash as representing, at best, minimum values.

Trace Elements in Coal

The analytical chemist has refined his art by the use of instrumental techniques such as neutron activation, atomic absorption, and mass spectrometry, to the point where he can identify any element in any sample that a geologist submits for analysis. Therefore, it is useless to list all the elements found in coal, for the only ones to be left off the list are those not as yet determined by the appropriate method.

Which elements are present in significant amounts in any sample may also depend on the bias of the sampler. Geologists are much more likely to be interested in the arsenic or mercury content of a coal if that coal is in the proximity of an arsenic or mercury ore deposit. For example, the Russian literature contains several analyses of mercury in coals of the Donetz Basin. These are relatively high values, and the Russian workers suggest that the mercury content of the coal may be used as a geochemical prospecting tool to aid in finding mercury deposits in the adjacent rocks. Similarly, the only mercury data on crude oil that I have seen published is from oil fields in California that are associated with mercury deposits. I am not aware of any published analyses of mercury in "normal" crude oils, and only recently have we at the Illinois Geological Survey worked on mercury content of "normal" coals.

Although virtually no statement can be made about the distribution of trace elements in coal that is not subject to exceptions, there are broad generalizations that have been repeated many times in review articles on mineral matter in coal.

Some elements (Ag, As, B, Be, Ga, Ge, Mo, Ni, Pb, and Y) appear to be enriched (relative to their concentration in the earth's crust, or the clarke) in almost all coal ashes studied. Other elements (Ba, Co, Cr, Cu, Mn, Sr, and V) are enriched in some ashes but by no means all.

Published ranges of any trace element show extremes. Examples are: germanium with a range of 7 to 11,000 ppm in coal; arsenic with less than 1 ppm in some coals to 8,000 ppm in some coal ashes, and beryllium with a range from less than 10 ppm to 8,000 ppm in coal.

Significance of Trace Elements in Coal

A. Coal as a source of useful metals. Before we proceed to a discussion of the deleterious and possible deleterious effects of trace elements in coal, we should mention the possible recovery of certain elements from coal. The annual world production and consumption of coal is in excess of 3×10^9 tons. Although this value multiplied by the trace element concentration can produce a large amount of any elements, the problem is one of recovery. Ga and Ge have been recovered from coal ashes. Lignite in North Dakota was mined for the uranium content of the coal ash--although most coals contain far below economic concentrations of uranium. Depending on a variety of economic factors, it has been suggested that Be, Ni, Zn, and Mo might also be recoverable from coal.

An economic factor has been recently introduced that may influence trace metal recovery. If the pressure for sulfur removal from the coal becomes great enough to make "chemical refining" of the coal necessary, recovery of several trace elements may be incorporated into the design of the coal treatment plants.

B. Deleterious effects of trace elements in coal. Trace elements in coals have been identified as the cause of a variety of untoward effects:

Arsenic, most likely present in the coals in association with pyrite, (FeS_2), has been found in coke and it can enter iron smelted with the coke. This embrittles the iron. Coal also has been used in the drying of hops in a malting kiln in the manufacture of beer. It has been suggested that the arsenic may find its way into the beer, and a detailed study of arsenic in beer was done at the turn of the century in England. This study exonerated the coal as a major source of the arsenic.

Other trace elements to be avoided in the manufacture of iron are gallium and germanium.

The effects of lead poisoning in both humans and livestock was reported in the 1930's from a coke works in England, and Be has been reported in the vicinity of coal-burning plants.

Arsenic, vanadium, and lead have been reported as concentrated in boiler deposits. These deposits are undesirable because they reduce the efficiency of the boiler and require periodic removal.

C. Mercury in coal.

The reason that we read about trace metals in coal in the Sunday supplements is not because of their effect on boiler deposits, the manufacture of steel, or even the brewing of better beers. Our interest is in the environment--air and water, principally--and the possible effects on the environment by large-scale burning of coal. Mercury is where it's at, or at least where it's been recently.

You have heard from Dr. John Wood about methylation of mercury, about the St. Clair River, and probably about Minimata, Japan. It occurred to some individuals (especially those being cited for polluting the Great Lakes), that there must be a large amount of mercury emitted from coal-burning power plants, and perhaps those that had been cited were not the only ones culpable. The question of possible mercury pollution from coal-burning power plants deserved an answer; but at that time (just about a year ago) no reliable data published, or unpublished, were avail able on the mercury content of coal.

The Illinois State Geological Survey was, at that time, conducting a study of the bottom sediments of Lake Michigan, and mercury was one of the elements being determined. Some results of this investigation are reported in the next section by H. V. Leland and N. F. Shimp. We modified the neutron activation analysis method that had been developed for the Lake Michigan samples and applied it to the analyses of mercury in coal. We recently published the results of the analyses of 55 raw coal samples of Illinois coals. The mean mercury concentration for all coals mined in Illinois is 0.18 ppm. Eleven samples of coals from states other than Illinois have mercury concentrations within the same range as Illinois coals, or slightly lower.

Three coal samples were individually separated into specific gravity fractions in the laboratory, and all exhibited a mercury reduction of at least 50 percent in the lightest coal fraction and a concentration of mercury in the heaviest fraction. A more detailed study of a single coal sample suggests that a significant part of the mercury is associated with the pyrite in the coal, and the remainder (perhaps up to 50 percent) is in organic association.

With regard to mercury in coal, we have what we feel are good and reliable data--since they are our data. But just where does that leave us? First, there is now an average figure available for someone to use in making estimates of the amount of mercury that is emitted from coal-burning power plants. But we still don't know if all the mercury is being emitted or if some is retained in the ash or boiler deposits.

A recent study, that has not yet been published, but has been reported on in the newspapers, has identified mercury in the gases emitted from the smokestacks of power plants. However, there were power plants where they did not detect mercury, and the amount estimated as an annual emission from at least one plant is unreasonably high, on the basis of our data on mercury in coal.

There is still the problem of ascertaining the significance of the available data. If we wish to play with the numbers, we can do as follows. If there are approximately 20 million tons of coal burned annually in the Chicago area, and if we assume an average mercury content for that coal (0.18 ppm), and if, assuming the worst possible situation, all the mercury is emitted to the atmosphere--then we would have 3.6 tons, or 7,200 pounds, of mercury emitted in the atmosphere in the Chicago area each year. (Incidentally, this much mercury would be worth approximately $28,800 at the going rate.) What, then, is the significance of these numbers? Certainly, 7,200 pounds of mercury is dangerous--if concentrated in one place. Getting run down by 3.6 tons of anything would hurt. If this was dumped directly into a water supply we would be certain of the tenor of our reaction. But if we have this much emitted in the Chicago metropolitan area over a year's time, should we be concerned? At the present time we don't see signs of mercury poisoning of people living in the vicinity of the power plants. The bottom sediments of the west side of Lake Michigan do not show an increase in mercury content near the top as they might if significant amounts of mercury were being added to it during the past 100-plus years of coal burning in the area.

Although there is certainly no basis for panic, additional data are required to complete the trace metal distribution pattern. The emission of smokestacks should be monitored and dispersion patterns of the elements should be outlined. This is true not only for mercury, but for other elements as well.

The data concerning mercury which we discussed are now available and recently an article on Se in coal has been published. These data provide a basis for further investigation and assessment of these elements in the environment. But our knowledge of the content of Cd, Be, Se, Sb, As, etc., in coal in general and in Illinois coals in particular varies from limited through negligible to none. Analyses of coals for these elements and studies to determine their modes of occurrence in coal are important first steps in ascertaining their possible deleterious effects.

Coal -- Why worry about it?

Thus far I have not presented much actual data on trace metals in coal, but have, rather, attemtped to provide a perspective for considering the problem. There is one last thought I would also like to include in this "perspective package." That is: Why should we be that concerned about coal? It contains sulfur which is emitted to the atmosphere when it is burned. It also produces oxides of nitrogen, and there just might be some ill effects from trace metals in the coal. One certain way to avoid these problems is to stop burning coal.

But, as Dr. Hubert E. Risser of the State Geological Survey recently pointed out, we have a present energy crisis, and we are confronted with serious shortages of both electrical generating capacity and fuels. Our demand for electric power has required a doubling of output every 10 years. Coal currently provides about half the energy consumed by electric utilities.

Coal is not the only source of energy beset with problems associated with the environment. Nuclear plants present problems of nuclear hazards, radio-active waste disposal, and thermal pollution. Some aspects of air pollution are shared by all forms of fossil fuels used for power generation. Even hydroelectric generation of power is coming under attack for altering the environment by the building of dams.

Most estimates of future energy demands project a much increased use of coal. The amount of energy in coal reserves of the United States far exceeds the energy stored in the reserves of the other fossil fuels. For some time to come, coal will be a major source of energy for the generation of electricity. The alternative is a cutback in power production with associated dire results. These results are not, as you might imagine, merely the curtailing of the use of electric toothbrushes, hair combs, dishwashers and hair dryers. From 65 to 70 percent of our electrical power generation goes to commercial and industrial users, and this is what would need to be reduced.

Conclusion

I was supposed to talk about trace metals in fossil fuels. However, I restricted the talk to coal. Also, I gave you precious little data on the concentrations of trace metals in coal. This is because of the difficulty in assessing the value of data on coal ash and not on whole coal, many of which were for tests made on samples of dubious origin, or at least on heavily biased samples.

However, the tools for doing these analyses on coal appear to be at hand and, most importantly, there are pressures, primarily from the public, that should enable research funds to be applied to the investigation of trace metals in coal, and, in the not too distant future, a presentation entitled "Trace Metals in Fossil Fuels" may actually be concerned with data on trace metals.

TRACE ELEMENTS IN SOUTHERN LAKE MICHIGAN

H. V. Leland and N. F. Shimp

Preface

This report on heavy metals and other trace elements in water, sediments and biota of southern Lake Michigan is a summary of information from numerous published and unpublished sources. Due to the scarcity of data from many elements and the diversity of sampling and analytical procedures employed, the findings of this review must be considered preliminary. The attempt in this report is to provide an appraisal of available data on trace element distributions in southern Lake Michigan and reference to pertinent publications.

Description of Lake Michigan

Lake Michigan is the third largest in surface area of the Great Lakes and lies completely within the United States. It is bordered by Michigan, Indiana, Illinois and Wisconsin; most of the 67,869 square-mile drainage area is in Michigan and Wisconsin. The basin topography is divided into five distinct areas: south basin, divide, north basin, straits area, and Green Bay (Figure 1). The mean depth of Lake Michigan is 276 feet, with maximum depths of 923 feet in the north basin and 550 feet in the south basin. The lake volume is estimated at 1,170 cubic miles.

The outflow of water from Lake Michigan is approximately the same as runoff from its drainage basin *(22)*. Although there are numerous tributaries flowing into Lake Michigan, none are large (over 5,000 cfs) and it has the smallest drainage of the Laurentian Great Lakes, 55,000 cfs at the Straights of Mackinac, and a small outflow through the diversion to the Chicago River.

The south basin, the portion of Lake Michigan described in this review, is defined as the area south of a line between Milwaukee, Wisconsin and Grand Haven, Michigan *(9)*. The natural northern limit of the south basin is the southern ridge of the divide, an area of resistent Traverse limestone *(31)*. The divide contributes to the partial isolation of subsurface waters of the south basin from the rest of the lake *(9)*. Since the average flow-through time of Lake Michigan is approximately 100 years *(24)*, the clearance time for substances discharged to the south basin must be even longer.

Despite the existence of several recent publications on Lake Michigan circulation *(1, 9, 22, 23, 17)*, the thoroughness of mixing in Lake Michigan or the south basin is not established. Vertical mixing is fairly complete, due to the physical overturning of the lake twice

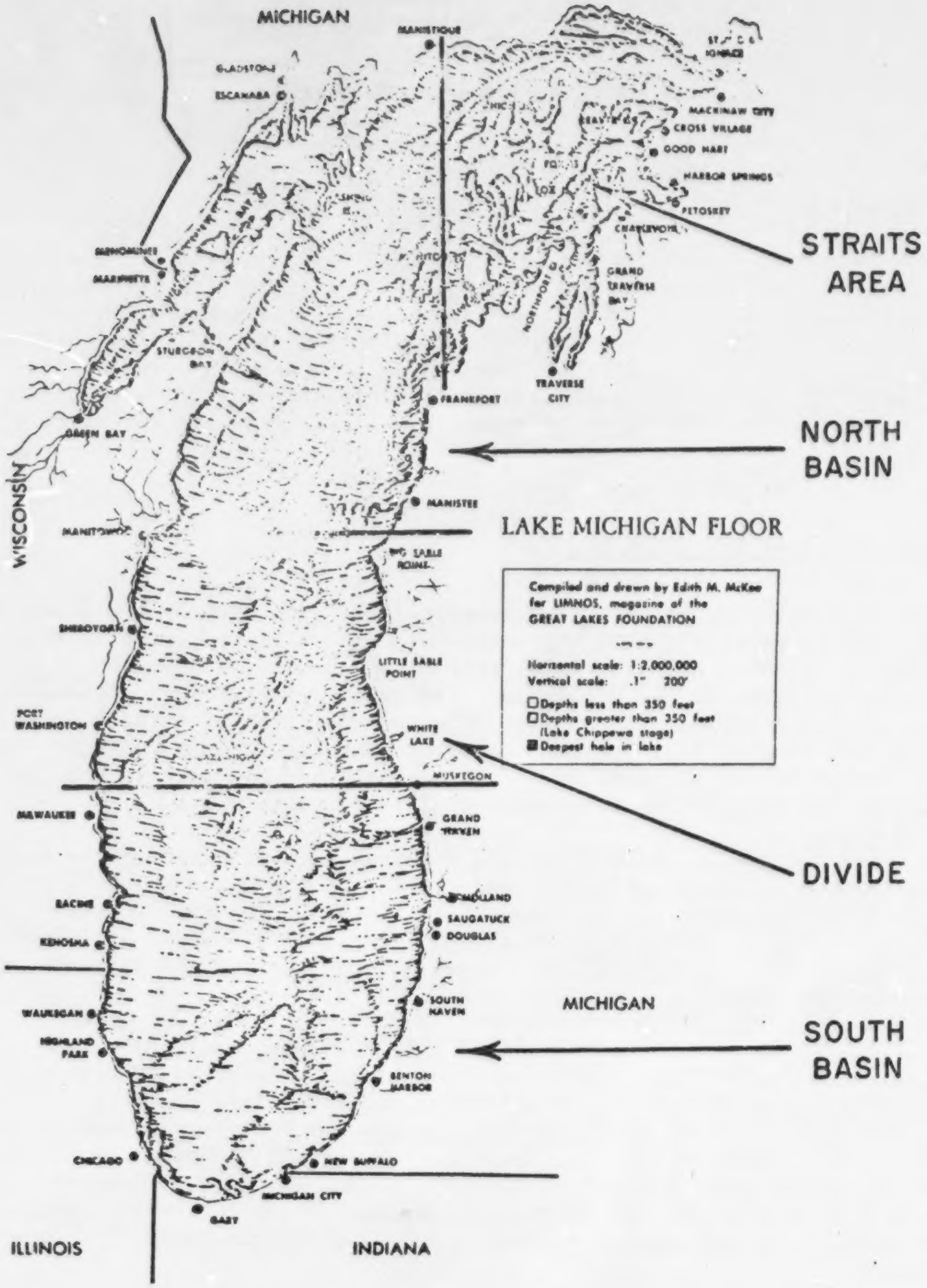

MICHIGAN
MANISTIQUE
GLADSTONE
ESCANABA
ST. IGNACE
MACKINAW CITY
CROSS VILLAGE
GOOD HART
HARBOR SPRINGS
PETOSKEY
CHARLEVOIX
STRAITS AREA
MENOMINEE
MARINETTE
GRAND TRAVERSE BAY
STURGEON BAY
TRAVERSE CITY
FRANKFORT
GREEN BAY
NORTH BASIN
WISCONSIN
MANISTEE
MANITOWOC
LAKE MICHIGAN FLOOR
BIG SABLE POINT
Compiled and drawn by Edith M. McKee
for LIMNOS, magazine of the
GREAT LAKES FOUNDATION
Horizontal scale: 1:2,000,000
Vertical scale: .1" 200'
☐ Depths less than 350 feet
☐ Depths greater than 350 feet (Lake Chippewa stage)
▨ Deepest hole in lake
SHEBOYGAN
LITTLE SABLE POINT
PORT WASHINGTON
WHITE LAKE
MUSKEGON
MILWAUKEE
GRAND HAVEN
DIVIDE
HOLLAND
RACINE
SAUGATUCK
DOUGLAS
KENOSHA
MICHIGAN
WAUKEGAN
SOUTH HAVEN
HIGHLAND PARK
SOUTH BASIN
BENTON HARBOR
CHICAGO
NEW BUFFALO
MICHIGAN CITY
GARY
ILLINOIS
INDIANA

Fig. 1. Basin topography of Lake Michigan *(9)*.

Table 1. Lake Michigan water quality in 1962-1963. *(10)*

(After FWPCA, 1968)

	Offshore			Inshore		
Parameter	No. of Samples	Average (mg/l)	Range (mg/l)	No. of Samples	Average (mg/l)	Range (mg/l)
Dissolved Oxygen	1,080	12	8.4-17	2,541	10	3.7-16
Percent Saturation	497	102	73-152	1,701	102	43-148
BOD	NS[a]	-	-	730	1.4	ND-8.6
NH_3-N	429	0.06	ND-050[b]	1,751	0.13	ND-1.4
NO_3-N	595	0.13	ND-0.65	1,654	0.14	ND-0.90
Organic-N	313	0.19	ND-0.52	529	0.21	0.01-0.70
Total Soluble PO_4	388	0.02	ND-0.14	1,382	0.04	ND-5.0
SiO_2	299	2.5	0.6-5.5	645	1.7	0.4-4.4
Na	321	3.9	2.7-6.5	400	4.0	1.8-7.5
K	325	1.1	0.4-2.0	453	1.2	0.5-3.8
Dissolved Solids	417	155	100-240	976	175	86-810
Specific conductivity (μ mhos/cm)	918	260	185-345	2,452	285	33-1130
pH (pH units)	1,040		7.5-8.9	2,113		6.4-9.3
Alkalinity	858	110	75-130	2,169	105	70-210
Ca	395	33	25-40	616	35	17-40
Mg	318	12	8-16	898	12	7-14
Cl	607	6.5	3.3-11	1,611	7.1	1.5-94
SO_4	561	20	12-30	1,547	20	10-76
Phenols (μg/l)	NS	-	-	1,033	2	ND-32

[a] NS - Not sampled.

[b] ND - Not detectable at sensitivity of test.

annually; but mixing of runoff from the watershed with the deeper waters is not understood quantitatively. At certain times, the currents of the inshore waters are largely independent of the general circulation of offshore waters. The inshore currents move parallel to the shoreline and with the prevailing wind, especially within the 30-foot depth contour *(11)*. Water quality conditions in inshore areas (less than 10 miles from shore) therefore may be considerably different from offshore conditions. Fee, Rousar and Zimmerman *(8)* found consistent differences in primary production, total phosphorus, nitrates and plant pigments between a station three miles from Milwaukee and other stations on a cross-lake run between Milwaukee, Wisconsin and Ludington, Michigan. The authors proposed that the differences are due to enrichment from Milwaukee and other population centers to the south since conditions at an inshore station at Ludington are very similar to the waterquality conditions of offshore stations.

The chemical characteristics of offshore waters of Lake Michigan are generally typical of oligotrophic lakes. Oxygen is always near saturation and the concentration of nitrogen (average of 0.13 mg per liter NO_3-N) and phosphorus (average of 0.02 mg per liter total PO_4) are generally low *(11)*. However, the water quality conditions of inshore waters near tributaries and major population concentrations are more variable (Table 1) and some areas have been classified as polluted *(10)*. The waters near Chicago are included in this category. Vaughn and Reed *(32)*, in a detailed report on the status of water quality of Lake Michigan at Chicago, concluded that improvements in bateriological quality and chemical parameters--including concentrations of ammonia and odors--occurred between 1969 and 1971. Two groups of water quality parameters did not improve during this period, however. The dissolved solids concentrations continued to increase, and the concentrations of total phosphorus and the numbers of phytoplankton were unchanged. Of particular concern were the data reported for total phosphorus in waters at Chicago. The median concentration for phosphorus in 1969 was 0.05 mg per liter total PO_4; in 1970 it was 0.06 mg per liter total PO_4. A concentration of 0.03 mg per liter total PO_4 is usually quoted as the threshold above which nuisance algal blooms may occur. In the years 1968-1970, 70 to 93 percent of the total phosphorus determinations in Lake Michigan waters at Chicago exceeded the threshold limit.

In a statement for the U. S. Department of Agriculture on sediment pollution of Lake Michigan, Cratty (1970) *(7)* identified by sub-basin the amounts of sediment contributed to Lake Michigan annually. The loss of sediment from sheet erosion, streambank erosion, and urban construction is particularly pronounced in the watershed of the south basin. Sheet erosion accounts for 95 percent of the addition. Of the two million tons of sediment delivered annually to Lake Michigan, more than one-half, or approximately 1.3 million tons, is derived from tributaries or urban complexes bordering the south basin. Roughly two-thirds of the annual sediment loss to the south basin is derived from watershed in Michigan.

The stratigraphy of unconsolidated sediments of Late Pleistocene Age in the southern part of Lake Michigan has been studied by Gross, *et al.*, (1970) *(16)* and Lineback, Ayer and Gross (1971) *(20)*. These sediments were divided into two major lithologic units. The upper unit is dominantly soft lacustrine clay of high water content; the lower unit consists of compact sandy sediments of glacial origin. Detailed descriptions of the various formations and their members are given for the two sedimentary units.

Distribution of trace elements in unconsolidated sediments of southern Lake Michigan

Recently deposited sediments are an integral part of the cycling of minerals in Lake Michigan. They provide a record of long-term environmental changes. The fine-grained sediments, which enter Lake Michigan through watershed erosion, reflect the lake environment at the time of deposition because of their capacity to incorporate or adsorb both inorganic and organic constituents from the water during transport and sedimentation. Study of the sediments, therefore, is basic to any comprehensive environmental investigation of Lake Michigan.

A series of reports presenting data on the distribution of 15 trace elements in southern Lake Michigan sediments was published by the Illinois State Geological Survey *(19, 25, 27, 28)*. Analyses were performed on sections of sediment cores and grab samples taken from approximately 50 locations in the south basin. Major constituents and other geochemical properties were also determined and will be described in future publications. Shipboard coring and sampling procedures were described by Gross, *et al.*, (1970) *(16)*, and Shimp, Leland and White (1970) *(28)*. Methods of analysis were described in the latter publications and others by Ruch, Kennedy and Shimp (1970) *(19, 25)*. For analysis of the sediments, optical emission (Pb, Cr, Be, Ni, and V), neutron activation (Br, Hg, As, Co, La, and Sc), atomic absorption (Cu and Zn), X-ray fluorescence (Mn), and colorimetric (B) methods were used. In addition to the trace element determinations, sediments were also analyzed for amounts of less than 2-micron clay size material and organic carbon. Precision for determination of the trace elements ranged between ±5 and ±20 percent; an indication of accuracy is given in Tables 2 and 3. Precision and accuracy for all determinations were considered good and well within the authors' ability to interpret results.

Examples of the distribution of trace elements and their relation to organic carbon and clay size material in selected sediment cores from southern Lake Michigan are shown in Figures 2-5. With the exception of copper, the concentrations of trace elements found to be accumulating in the uppermost, or surficial, fine-grained sediments were more closely related to amounts of organic carbon than to amounts of iron oxides, manganese oxides, clay-size material, or water depth. Correlation coefficients for accumulating trace elements of surficial sediments versus the organic carbon content were as follows: arsenic, 0.72; bromine, 0.77; chromium, 0.80; copper, 0.49; mercury, 0.71; lead, 0.86; and zinc,

Table 2. Comparison of optical emission trace element values with USGS standard rock values (ppm).

	BASALT BCR - 1		GRANITE G - 2		GRANODIORITE GSP - 1		ANDESITE AGV - 1	
	USGS*	ISGS†	USGS	ISGS	USGS	ISGS	USGS	ISGS
Cr	16	10.4	9	11	13	14	13	12
Pb	18	17	29	34	52	64	35	37
Be	2.6	3.5	2.4	1.1	0.8	0.9	1.8	1.8
V	384	240	37	28	52	48	121	78
Co	36	25	4.9	4.8	7.5	10.6	15.5	13
Ni	15	10	6.4	3	11	11	17.8	18

* USGS, Flanagan (1969)

† ISGS, Illinois State Geological Survey Analyses by J. A. Schleicher

Table 3. Comparison of neutron activation values for arsenic and mercury in USGS standard rock W-1 (values in ppm of air-dried sample)

	As	Hg
U. S. Geological Survey	2.4*	0.17, 0.34**
Illinois Geological Survey	2.3†	0.25††
Precision Illinois Geological Survey	± 7% †	± 20%††

* Fleischer (1969)

** Fleischer (1965)

† Ruch, Kennedy and Shimp (1970)

†† Kennedy, Ruch and Shimp (1971)

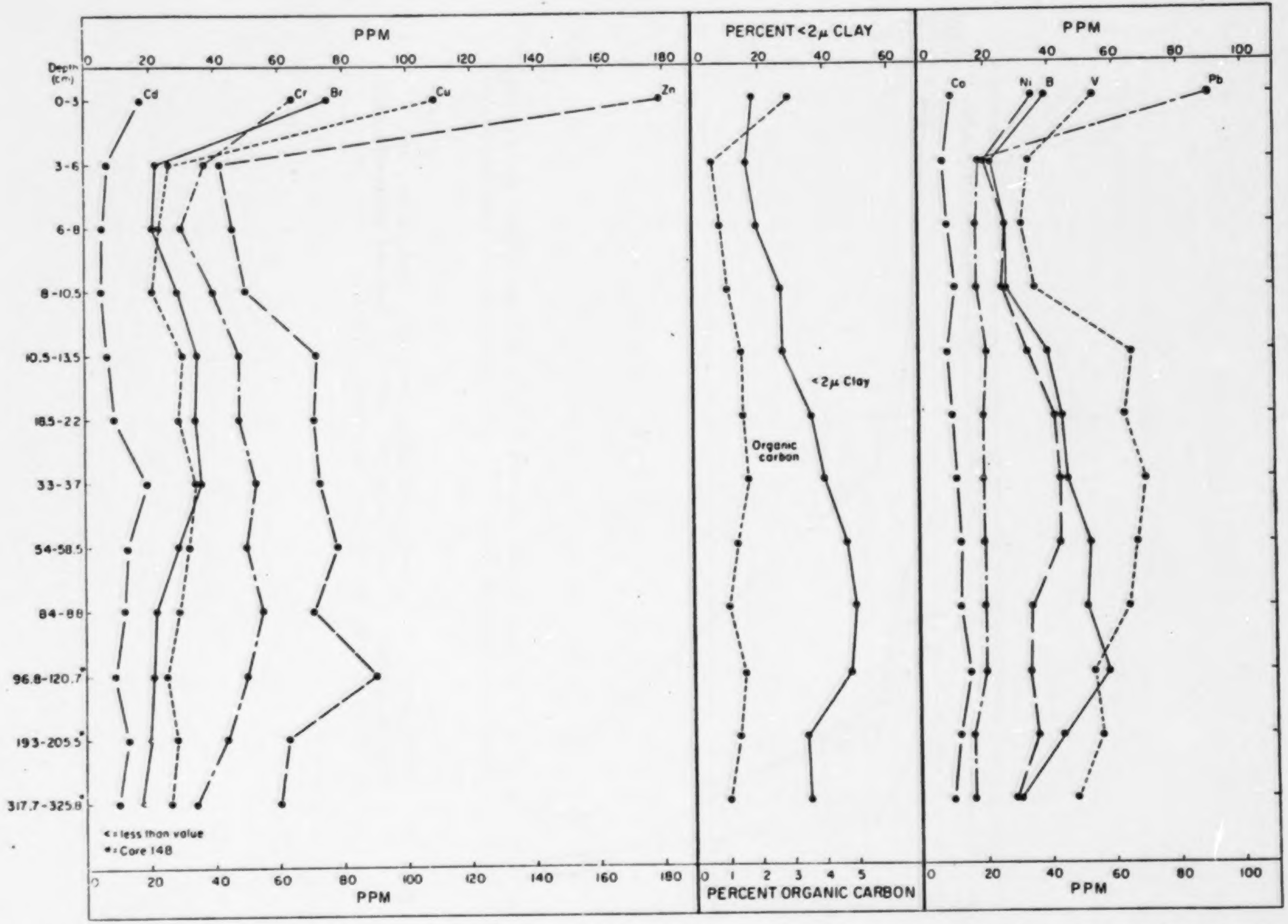


Fig. 2. Distribution of trace elements, organic carbon, and <2-micrometer clay in Lake Michigan cores No. 44 and 148 located approximately 12 miles off Waukegan, Illinois *(28)*.

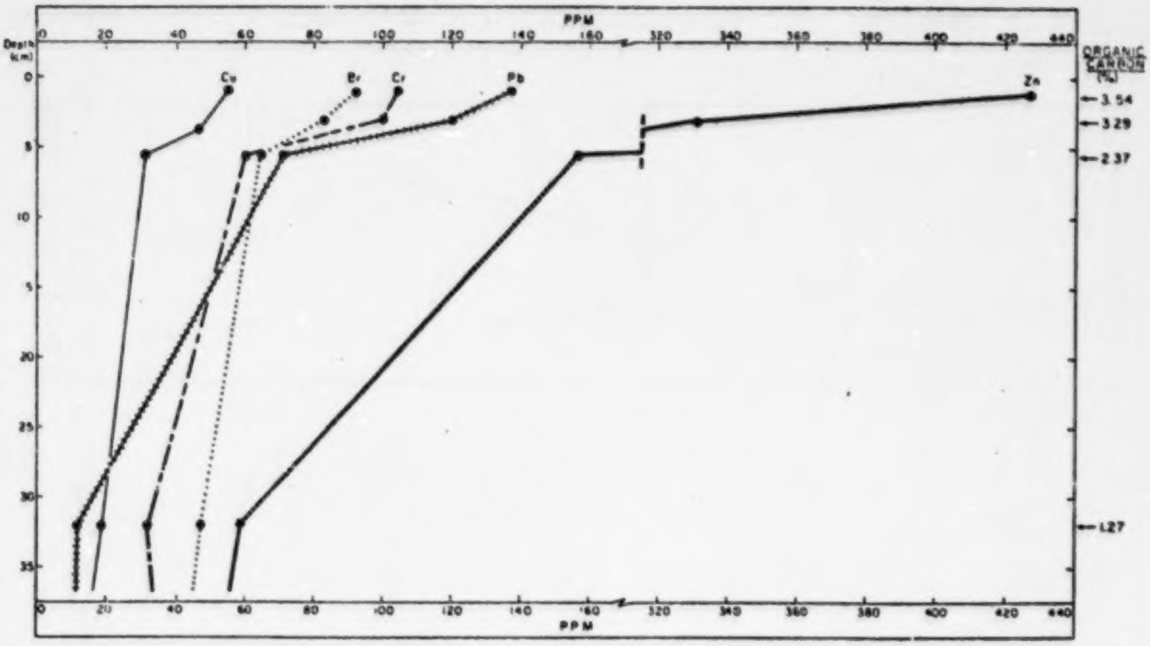


Fig. 3. Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 113 located approximately 13 miles off Benton Harbor, Michigan. *(27)*

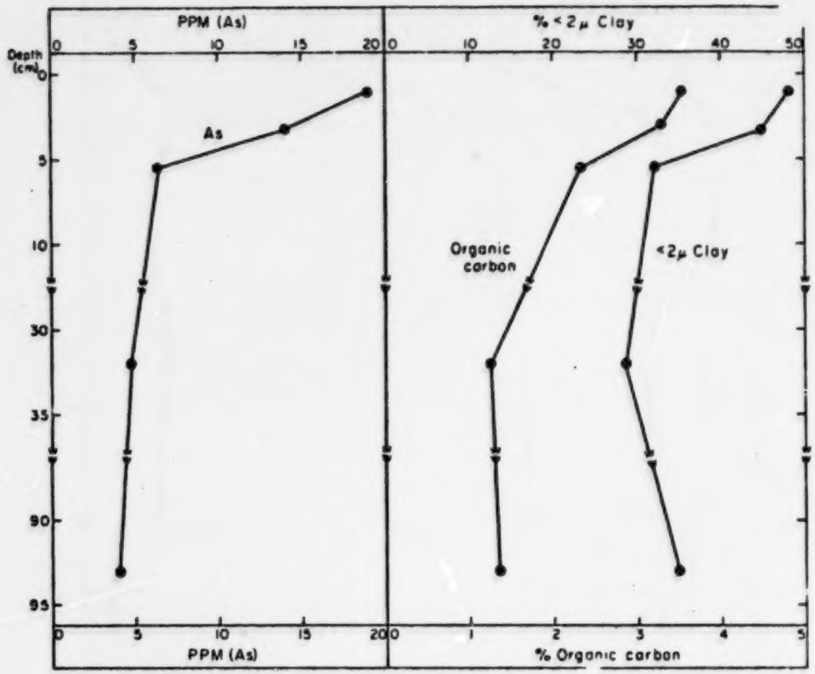


Fig. 4. Distribution of arsenic, organic matter, and <2 micrometer clay in Lake Michigan core 113 located approximately 13 miles off Benton Harbor, Michigan. (27)

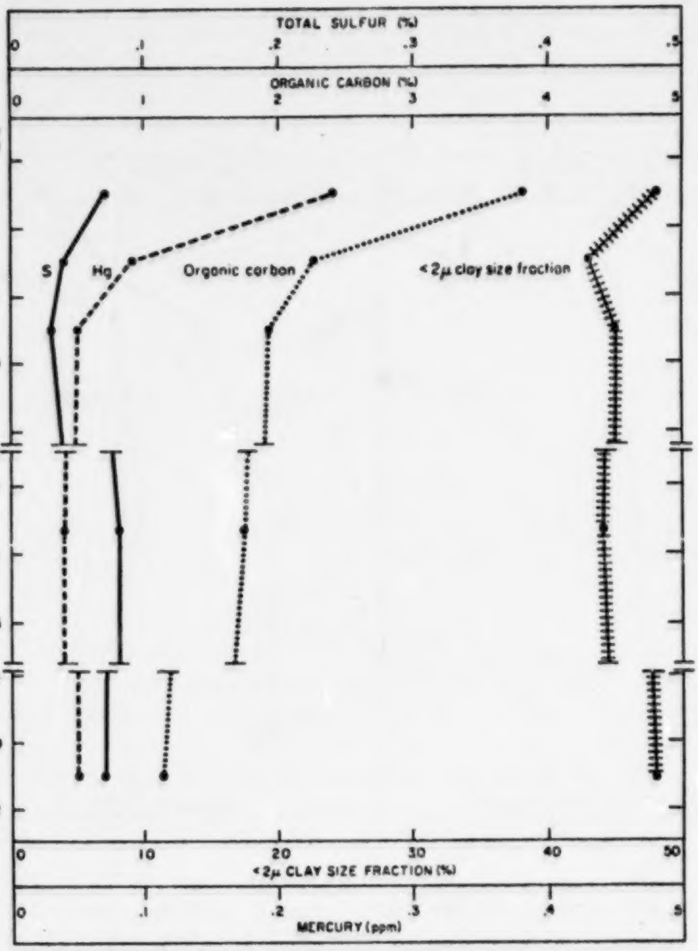


Fig. 5. Distribution of mercury, organic carbon, total sulfur, and <2-micrometer clay size fraction in Lake Michigan core 115 located approximately 16 miles off Benton Harbor, Michigan *(19)*.

0.73. In contrast, concentrations of elements not accumulating in the sediments were poorly correlated with organic carbon.

The concentrations of lead (Fig. 6), zinc (Fig. 7), and mercury (Fig. 8) illustrate the pattern of deposition of trace elements in sediments of Lake Michigan's south basin. Similar distribution patterns were found for arsenic, bromine, copper and chromium. The following is a brief summary of results:

(a) Of the 15 trace elements determined in sections of 20 cores (approximately 100 samples) and 30 grab samples from southern Lake Michigan, bromine, mercury, arsenic, lead, copper, chromium, and zinc are accumulating in the uppermost portions (0-10 cm) of the organic-rich fine-grained sediments.

(b) Trace elements exhibiting little or no enrichment near the sediment-water interface are boron, beryllium, cobalt, lanthanum, manganese, nickel, scandium, and vanadium.

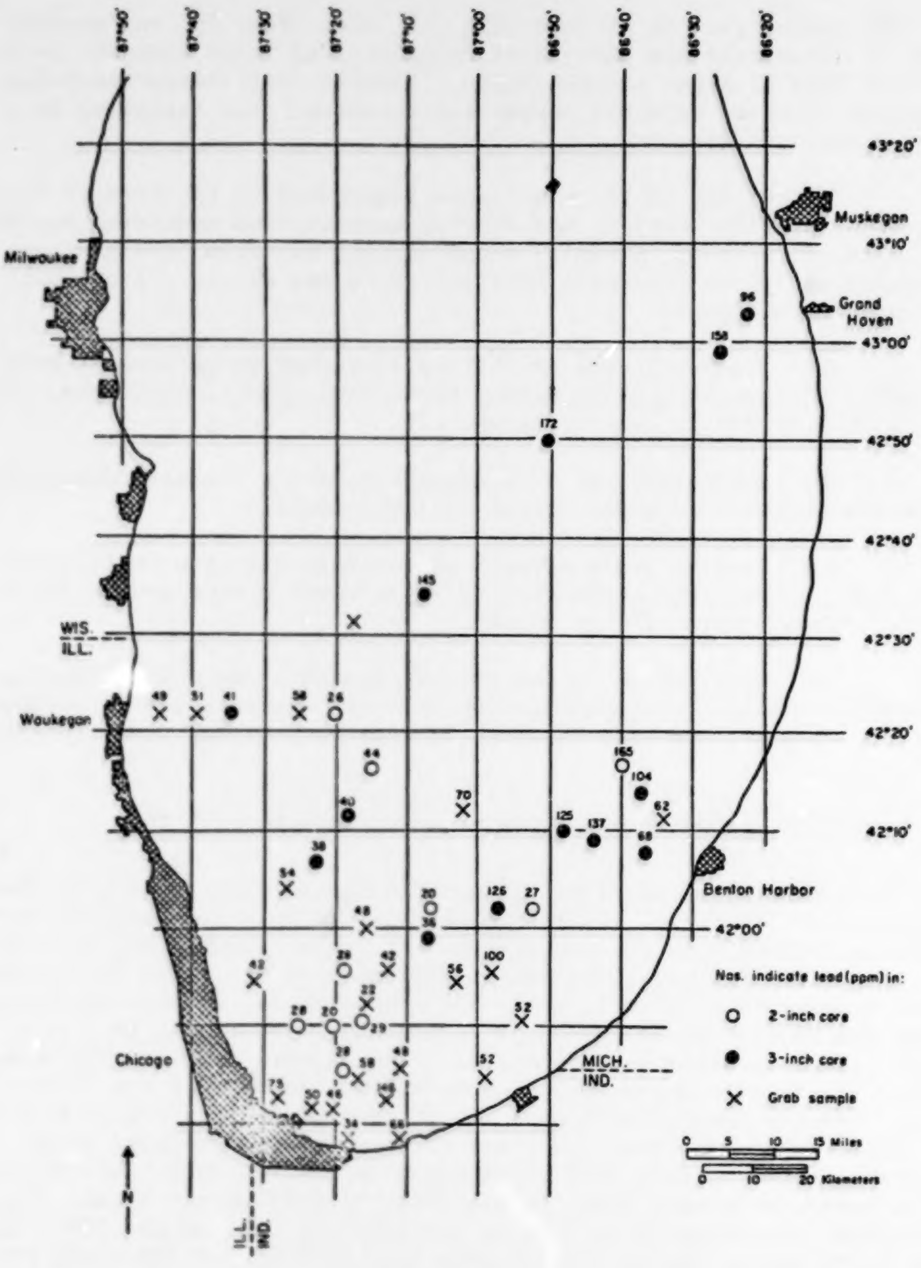
(c) Concentrations of accumulating trace elements generally correlate best with organic carbon concentrations.

(d) Largest trace element accumulations in the south basin of Lake Michigan occur in sediments off major river mouths and in the central or deepest parts of the basin.

(e) Sandy areas in the extreme southern end of Lake Michigan generally contain low concentrations of trace elements and no accumulation of trace elements has been observed in sediments at the water interface.

Trace elements in water and biota of southern Lake Michigan

Data sufficient to permit materials-balance studies of Lake Michigan currently do not exist. Published information on trace elements is especially limited; but the contribution of surface runoff and industrial discharge to heavy metal and other trace element pollution in the south basin appears to be significant. The Environmental Protection Agency (then the Federal Water Pollution Control Administration), in a study of major rivers entering Lake Michigan, found copper, cadmium, chromium, nickel and zinc in appreciable concentrations in many of the tributaries *(10)*. Cadmium concentrations in the St. Joseph River averaged 0.02 mg per liter, which is twice the limit recommended for drinking water. Chromium concentrations of 0.04 mg per liter, which were found in the Grand River, were very close to the limit of 0.05 mg per liter. Copper concentrations ranged from 0.06 mg per liter to 0.15 mg per liter in some tributaries; concentrations less than 0.02 mg per liter may be harmful to aquatic life. Such levels of potentially toxic elements indicate serious impairment of water quality. Copper, cadmium, chromium, nickel, lead and zinc are also present in streams and harbors in the Illinois River basin in amounts exceeding recommended limits (Environmental Protection Agency, unpublished data).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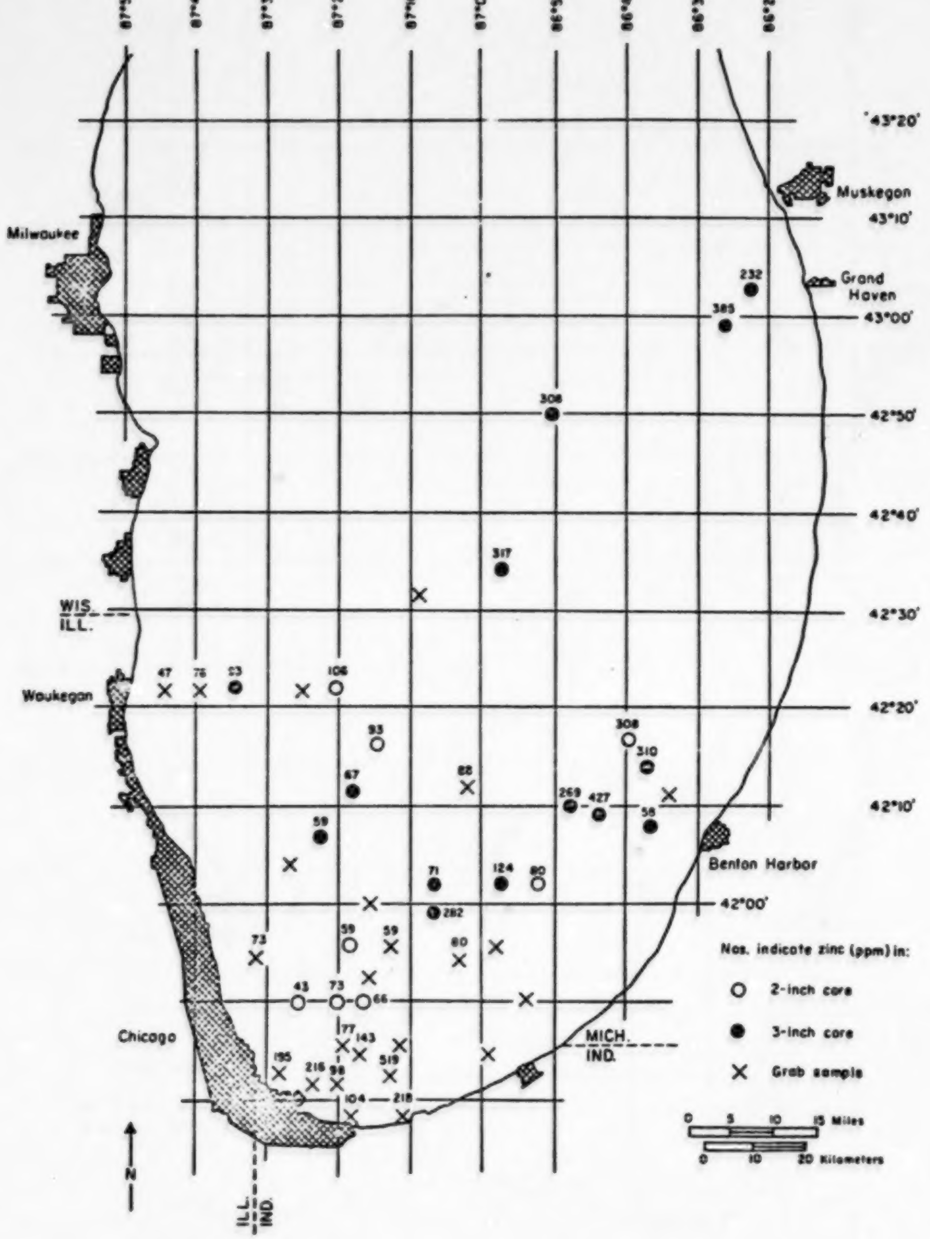
Nos. indicate lead (ppm) in:
○ 2-inch core
● 3-inch core
× Grab sample
0 5 10 15 Miles
0 10 20 Kilometers

Fig. 6. Concentration (ppm) of lead in the most recent sediments of southern Lake Michigan *(27)*.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71
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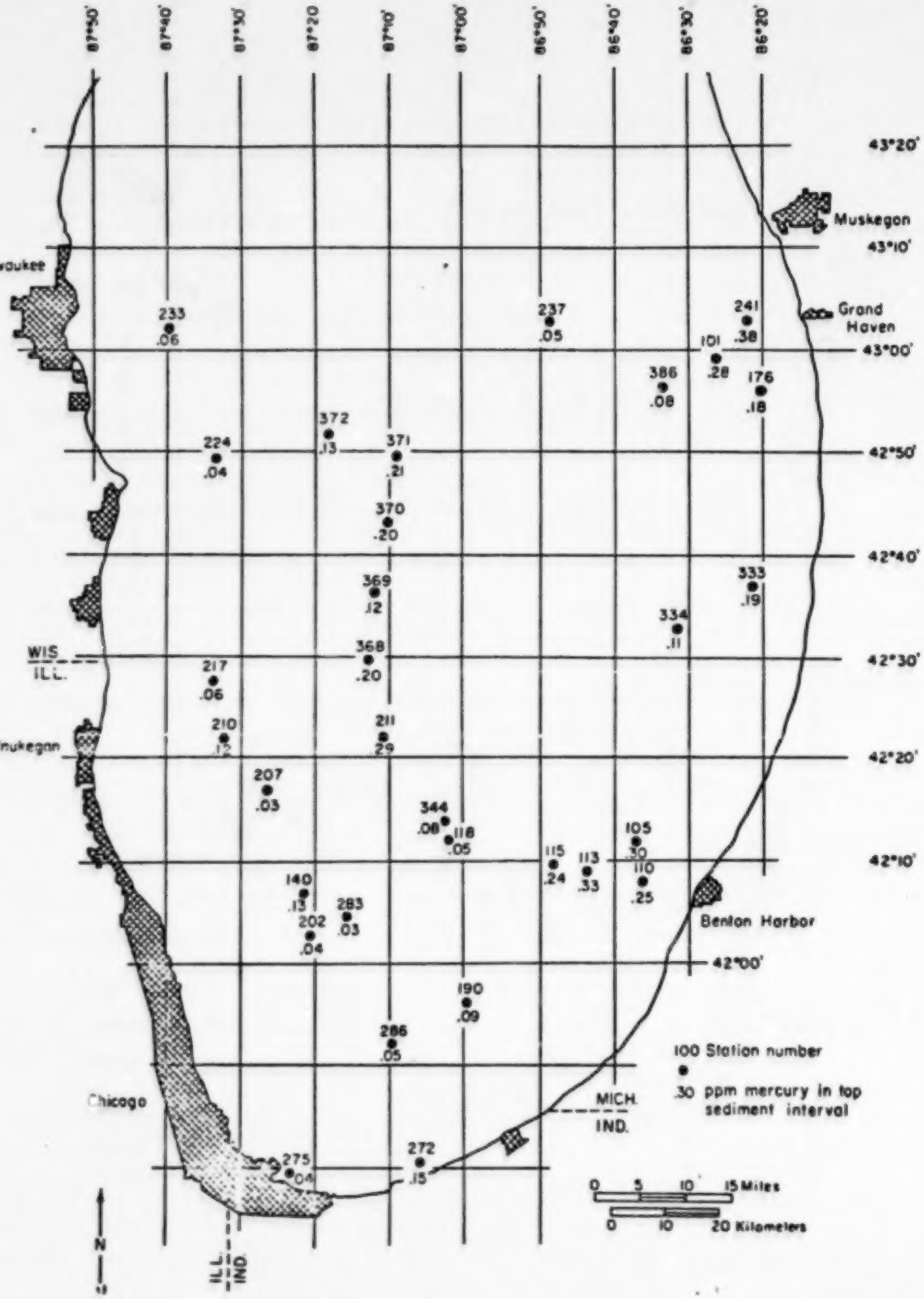
66
77
143
195
216
98
519
104
218
Nos. indicate zinc (ppm) in:
○ 2-inch core
● 3-inch core
× Grab sample
0 5 10 15 Miles
0 10 20 Kilometers

Fig. 7. Concentration (ppm) of zinc in the most recent sediments of southern Lake Michigan *(27)*.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Waukegan
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237 .05
241 .38
101 .28
386 .08
176 .18
372 .13
371 .21
224 .04
370 .20
369 .12
333 .19
334 .11
368 .20
217 .06
210 .12
211 .29
207 .03
344 .08
118 .05
105 .30
115 .24
113 .33
110 .25
140 .13
283 .03
202 .04
190 .09
286 .05
275 .04
272 .15
100 Station number
.30 ppm mercury in top sediment interval
0 5 10 15 Miles
0 10 20 Kilometers

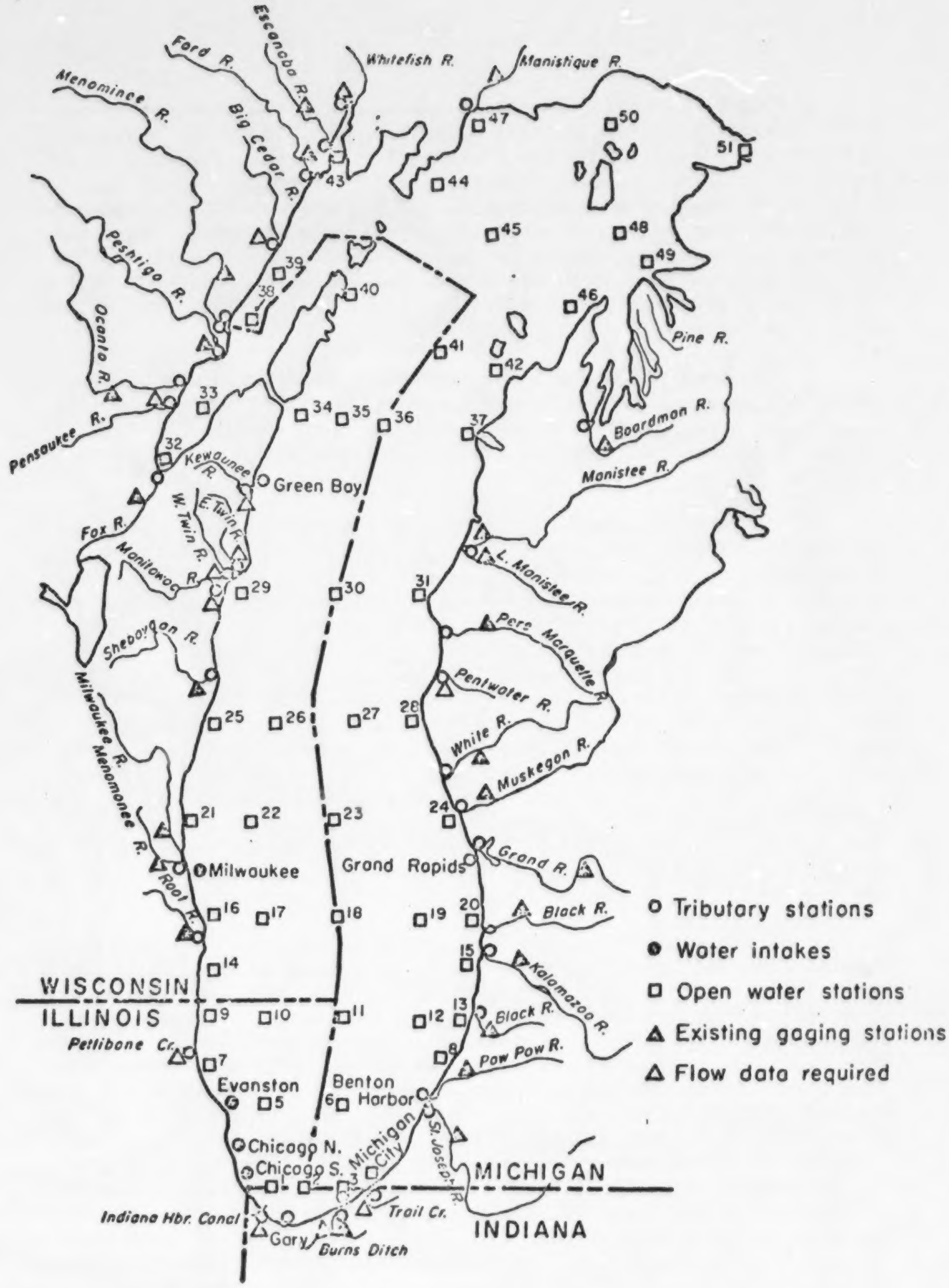
Fig. 8. Sample locations and mercury content of the top interval of sediment at each location *(19)*.

In 1968 a Monitoring Committee representing the five conferees (Federal Water Pollution Control Administration, Illinois, Indiana, Michigan and Wisconsin) at the first session of the Conference on the Matter of Pollution of Lake Michigan and Its Tributary Basin, was appointed to develop recommendations for a coordinated State-Federal program for monitoring the water quality of Lake Michigan. Pertinent recommendations of the Committee, which were subsequently adopted by the conferees at the second session of the Conference on the Matter of Pollution of Lake Michigan and Its Tributary Basin (1969), may be summarized as follows:

1. Each state should monitor designated tributary streams near the points of discharge to Lake Michigan (Fig. 9) for the purpose of determining constituent loadings. Tributary water samples should be collected at least monthly and analyzed for specific quality parameters (Table 4).

2. The Environmental Protection Agency should appraise the quality of the open waters of Lake Michigan (the 51 station locations indicated in Fig. 9) each spring, summer and fall. The 22 parameters selected by the Monitoring Committee to evaluate water quality at each station are the following: ammonia, calcium, chloride, true color, dissolved oxygen, magnesium, nitrate, organic nitrogen, pH, total phosphorus, phytoplankton, potassium, gross α-radiation, gross β-radiation, silica, sodium, dissolved solids, suspended solids, sulfate, total plate count, turbidity and zoo-plankton. Determinations of heavy metals in the open waters are not recommended routinely, but water and sediment samples should be analyzed for copper, chromium, cadmium, lead, nickel and zinc every five years to detect any accumulation of these elements in the lake. After two years of data collection the information should be evaluated to determine if specific water quality measurements can be eliminated or if additional determinations are required.

Since the adoption of the Committee's recommendations in 1969, several findings have emphasized the importance of a continuing water quality evaluation of Lake Michigan and the need to include measurements of certain heavy metals in the monitoring program. In 1970 numerous instances were reported of mercury pollution in the Great Lakes region and commercial fishing was consequently banned in Lake St. Clair and Lake Erie. Great concern has been expressed by the public and by government at several levels regarding the hazards of this element. An immediate need exists for reliable data on sources of mercury in the Lake Michigan watershed, its distribution if released into the environment, and its ecological significance where concentrated in lake sediments. In addition, recent studies of the accumulations of arsenic, bromine, chromium, copper, lead, mercury, nickel and zinc in the sediments of southern Lake Michigan indicate that substantial quantities of elements that are toxic to aquatic life at very low concentrations in water enter the lake from the surrounding watershed. Finally, despite considerable effort at locating sufficient sources of data, meaningful materials-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Manistique R.
Menominee R.
Big Cedar R.
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Peshtigo R.
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Pine R.
Oconto R.
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Boardman R.
Pensaukee R.
32
Kewaunee R.
Green Bay
Manistee R.
Fox R.
E. Twin R.
W. Twin R.
L. Manistee R.
Manitowoc R.
29
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Pere Marquette R.
Sheboygan R.
Pentwater R.
Milwaukee R.
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White R.
Muskegon R.
Menomonee R.
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Milwaukee
Grand Rapids
Grand R.
Root R.
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Black R.
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Kalamazoo R.
WISCONSIN
ILLINOIS
9
10
11
12
13
Black R.
Pettibone Cr.
7
8
Pow Pow R.
Evanston
5
Benton Harbor
6
Chicago N.
Michigan City
St. Joseph R.
Chicago S.
1
2
3
4
MICHIGAN
Indiana Hbr. Canal
Trail Cr.
Gary
Burns Ditch
INDIANA
○ Tributary stations
● Water intakes
□ Open water stations
▲ Existing gaging stations
△ Flow data required

Fig. 9. Recommended water quality monitoring stations *(3)*.

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Table 4. Recommended analytical schedule for tributary monitoring stations *(3)*.

	Parameters / Tributary Monitoring Stations	ILL.	INDIANA			MICHIGAN																		WISCONSIN											
		Pettibone Creek	Burns Ditch	Trail Creek	Indiana Harbor	Big Cedar River	Black River-Holland	Black River S.Haven	Boardman River	Escanaba River	Ford River	Grand River	Kalamazoo River	Manistee River	Manistique River	Menominee River	Muskegon River	Pentwater River	PereMarquette River	Pine River	St. Joseph River	[illegible]nite River	Whitefish River	East Twin River	Fox River	Kewaunee River	Manitowoc River	Menominee River	Milwaukee River	Oconto River	Pensaukee River	[illegible]	Root River	Sheboygan River	West Twin River
1	Alkalinity, Total as $CaCO_3$	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
2	Alkalinity, P, as $CaCO_3$*																							M	M	M	M	M	M	M	M	M	M	M	M
3	Biological Oxygen Demand, BOD5	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
4	Cadmium**	M					M	M				M	M	M		M	M		M		M	M			M		M		M						
5	Calcium*		Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q												
6	Chloride	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
7	Chromium**	M	M		M		M	M				M	M	M		M	M		M		M	M			M		M		M						
8	Color*		T	T	T																			M	M	M	M	M	M	M	M	M	M	M	M
9	Conductivity*	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M												
10	Copper**	M	M		M		M	M				M	M	M		M	M		M		M	M			M		M		M						
11	Cyanide**	M	M		M		M	M				M	M	M		M	M		M		M	M			M		M		M						
12	Dissolved Oxygen, DO	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
13	Fluorides*	M			M		M	M				M	M	M		M	M		M		M	M			M		M		M						
14	Hardness, as $CaCO_3$	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
15	Iron, Total**	M	M	M	M		M	M		M		M	M	M		M	M		M		M	M			M		M		M						
16	Lead**	M					M	M				M	M	M		M	M		M		M				M		M		M						
17	Magnesium*					Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q												
18	Manganese**	M	M		M		M	M				M	M	M		M	M		M		M	M			M		M		M						
19	MBAS*	M																																	
20	Nickel**	M	M		M		M	M				M	M	M		M	M		M		M	M			M		M		M						
21	Nitrate - Nitrite as N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
22	Nitrogen, Ammonia as N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
23	Nitrogen, Organic as N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
24	pH (field determination)	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
25	Phenolic Compounds**	M	M	M	M		M	M				M	M	M		M	M		M		M	M			M		M		M						
26	Phosphorus, Soluble as P*					M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
27	Phosphorus, Total as P	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
28	Potassium*		Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q												
29	Radiation, Gross Alpha*	M																							M			M	M						
30	Radiation, Gross Beta*	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M		M			M	M						
31	Sodium*		M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M												
32	Solids, Dissolved	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
33	Solids, Suspended	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
34	Solids, Volatile Suspended	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
35	Sulfate**	M	M	M	M					M		M	M	M	M	M	M				M	M			M			M							
36	Temperature	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
37	Turbidity*	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M												
38	Zinc**	M	M		M							M	M	M		M	M		M		M	M			M		M		M						
39	Fecal Coliform	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
40	Total Coliform	M	T	T	T	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

Analytical Frequency: M - Monthly, T - Twice Monthly, Q - Quarterly *Optional **Where Appropriate balance studies of the waters of Lake Michigan are at present impossible (Ayers, 1970). Such data are required for an evaluation of the capacity of the lake to absorb domestic, industrial and agricultural wastes without further deterioration.

Published trace element concentrations for waters of Lake Michigan are scarce and data that are available must be evaluated with caution. Concentrations are generally low (less than 0.1 to 10 µg per liter) and the samples are easily contaminated at the time of collection and analysis. Furthermore, trace element concentrations in water may change rapidly after sampling, due to precipitation or adsorption. A summary of data obtained from investigations in which precautions sufficient to avoid sample contamination were thought to be employed are presented in Table 5 to indicate the approximate concentrations of trace elements in Lake Michigan. Variations in trace element concentrations related to season, water depth and sample location occur. The highest concentrations of each element are near large metropolitan areas and major river mouths.

The following analytical procedures were used for the trace element determinations reported:

Lake Michigan Survey (Ayers, 1970). Atomic absorption was employed without prior sample concentration for determinations of Sr and Zn. Measurements of Ba, Cd, Co, Cu, Fe, Pb, Mn, Mo and Ni were made by atomic absorption following sample concentrations by low temperature and low pressure sublimation. One liter of acidified, filtered (0.45 µ) lake water was evaporated to dryness and the residue dissolved in 10 ml of 10-percent nitric acid.

City of Chicago, Department of Water and Sewers. Atomic absorption was employed for the determination of Cr, Cu, Pb, Ni and Zn in unfiltered lake water. The elements were chelated with ammonium pyrrolidine dithiocarbamate, which was then extracted from the sample with methyl isobutyl ketone *(12)*, giving a 20-fold concentration. Determinations of Cd, Co and Mn were made by atomic absorption, following evaporation of the sample. Mercury was determined by flameless atomic absorption.

Environmental Protection Agency. Determinations of Cd, Cr, Cu, Pb, Mn, Zn, and Ni were made by atomic absorption on unfiltered, acidified lake water after concentrating the sample five-fold by evaporation.

University of Illinois. Determinations of Cd, Co, Cu, Pb and Zn were made by atomic absorption on filtered (0.45 µ), acidified lake water. The elements were chelated with ammonium pyrrolidine dithiocarbamate, which was then extracted from the sample with methyl isobutyl ketone, giving a 15-fold concentration. Vanadium determinations were made by atomic absorption after extraction with butylacetate *(2)*. Iron was measured colorimetrically *(30)*.

Few published data on trace elements in Lake Michigan biota currently exist. The values reported (Table 6) are much higher than concentrations found in waters of Lake Michigan, and the trace elements are concentrated selectively by organisms. The samples of plankton and benthos were contaminated to an unknown degree with sediment *(1)*, and no attempt was made to measure the portion of trace elements contributed by adsorption. Consequently, the enrichment factors reported must be considered maximum values. Enrichment factors for copper, iron, manganese and zinc in Lake Michigan plankton are roughly equivalent to enrichment factors reported for shellfish in marine environments.

Examination of trace element concentrations in biota of different areas of Lake Michigan may help identify major sources of certain elements. The highest concentrations of selenium in zooplankton occur near Chicago, Illinois, and Milwaukee, Wisconsin. A decrease in selenium occurs in the direction of the prevailing winds, indicating an air-borne route of entry. Concentrations of mercury in zooplankton are highest near shore and near river mouths *(6)*. Pontoporeia affinis, a benthic amphipod distributed in most areas of Lake Michigan, is a suitable monitor organism for manganese-54 and zinc-65, but not for isotopes of strontium *(18)*. The suitability of P. affinis and other aquatic organisms for localized use as monitor organisms warrants further study.

Table 5. Trace element concentrations in Lake Michigan water in 1969-1970.

	Lake Michigan Survey (Ayers, 1970) [a]	Chicago Water Supply Div. of Water Purification Dept. of Water and Sewers		Lake Michigan Basin Office Open-Lake Survey E. P. A.	Southern Lake Michigan Survey (Univ. of Illinois)[b]	
Element	Average (μg/l)	Average (μg/l)	Range (μg/l)	Range (μg/l)	Average (μg/l)	Range (μg/l)
Arsenic	2.3 (max.)*	< 1	(<1)[c]			
Barium	26*					
Cadmium	1.0*	< 1	< 0.5-4	< 0.1-2.2		< 0.1-1.0
Chromium			< 0.5-19	0.8-70		< 0.5-10
Cobalt	1.5	2	< 0.5-6		< 1	(< 1)[c]
Copper	2.7*	1-3	0.5-46	< 1-10	2.2	0.6-16
Iron	7.2*	0.02 mg/l	<.005-.05 mg/l		6	4-38
Lead	0.2*	< 0.5-2	< 0.5-20	< 1-9.8	< 1	0.2-4
Mercury		< 0.1	<(0.1)[c]	(<0.5)[c]		
Molybdenum	1.5					
Nickel	2.3	4	< 0.5-10	< 1-7		
Strontium	112					
Vanadium					< 0.05	
Zinc	32.4*		< 0.5-20			< 5-30

[a] Data indicated by an asterisk were contributed by V. S. Hastings, Commonwealth Edison Company. Maximum concentrations of the elements for which averages are given were generally no more than double and not more than three times average values. Results not indicated by an asterisk were obtained from samples taken at a single offshore station in southern Lake Michigan.

[b] Iron determinations contributed by L. M. Henley, Illinois State Water Survey. The other determinations were contributed by J. L. Clement, Department of Civil Engineering, and A. M. Hartley, Environmental Research Laboratory, University of Illinois.

[c] Limit of sensitivity of the method.

Table 6. Selected trace element concentrations in biota of Lake Michigan.

Element	Phytoplankton (µg/g-dry tissue)[a]		Zooplankton (µg/g-dry tissue)		Benthos (µg/g-dry tissue)		Fishes (Ng/g-dry tissue)[b]
Arsenic				(3500)			3 - 43 ± 12
Barium		(937)		(473)	20.3 ± 1.7	(985)	< 200
Bromine		(4730)		(6630)		(5000)	
Cadmium							62 ± 15 - 76 ± 8
Chromium	2.36 ± 1.18		5.88 ± 2.61		2.51 ± 1.26		900 ± 500 - 1600 ± 200
Cobalt		(207)		(123)		(109)	24 ± 2 - 42 ± 15
Copper	28.1 ± 1.5	(14,500)	28.8 ± 0.4	(14,800)	24.0 ± 1.5	(12,400)	800 ± 150 - 2700 ± 600
Iron	166 ± 6	(36,000)	110 ± 5	(26,800)	112 ± 7	(20,100)	
Manganese	10.6 ± 0.6	(14,100)	17.0 ± 0.4	(11,900)	13.7 ± 0.6	(31,100)	
Mercury	1 - 14[c]	(> 10,000)	1 - 14[c]	(> 10,000)	1 - 6[c]	(> 10,000)	130
Selenium	0.5 - 6[c]		0.5 - 6[c]		1 - 4[c]		
Strontium	15.1 ± 1.4				49.5 ± 1.3		
Zinc	88.4 ± 5.9	(2710)	104 ± 3	(3550)	66.9 ± 6.1	(3670)	

[a] Trace element concentrations in phytoplankton, zooplankton and benthos are from Ayers (1970). Values in parentheses are enrichment factors as computed against the concentration of the element in Lake Michigan Water. The samples were lightly contaminated with sediment.

[b] Trace element concentrations in whole fish are from Lucas, Edgington and Colby (1970) with the exception of the value for mercury which is an average for fishes of Lake Michigan (Edington, unpublished data).

[c] Data for mercury and selenium are from Copeland (1970).

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REMOVAL OF TRACE METALS FROM PUBLIC WATER SUPPLIES

B. B. Ewing

Environmental pollution by trace metals assumes many forms in touching the lives of people. One intimate contact people have with their environment is the water they drink, the water they wash in, the water they use for their recreation, and the water they use for their livelihood. The effects of trace metals may be detrimental or beneficial and may vary greatly, depending upon the particular trace metal involved, the chemical and physical form of the metal, the concentration in which it occurs, and the use to which the water is put. There are occasions where the effect would be detrimental and in which removal is justified by health or economic considerations. Methods for removal of excessive concentrations of most of these trace metals are available and can be applied either in the treatment of wastewaters before disposal to the environment, to public water supplies prior to distribution to the public, or by the industrial or domestic consumer.

Table 1 illustrates some of the effects of trace metals in water. There are many which are primarily of concern because of their toxicity. This includes arsenic, barium, cadmium, the hexavalent form of chromium, lead, selenium, silver, and (recently added to the list) mercury. As such, they are of significance in low concentrations in public water supplies which are used partly for drinking water and in surface waters used for aquatic life. The drinking water standards provide limits for these metals because of their toxicity.

Some of the other metals, such as copper, iron, manganese and zinc, are lower in toxicity but are important for other reasons. All four of these metals may produce a metallic or astringent taste even in low concentrations in drinking water or in beverages. Iron and manganese cause color problems when the oxidized form produces red or black precipitates which stain clothing and porcelain plumbing fixtures, or interfere with use in paper, textile and beverage industries. Iron and manganese can also be quite troublesome due to their tendency to support the growth of autotrophic microorganisms, forming slimes which tend to clog filters and pipes in water distribution and plumbing systems or produce unaesthetic appearance in water drawn from the tap when these slimes break up and slough off. In addition, it has been reported that the presence of dissolved copper greatly accelerates the corrosion of iron and galvanized iron pipe. Zinc has an additional effect of being a mild irritant to the gastrointestinal tract.

The U. S. Public Health Service has established Drinking Water Standards based primarily upon health considerations which apply to water provided for drinking on interstate carriers. Certainly the quality requirements imposed by drinking water are among the most stringent and they often tend to govern the quality of treated water for public water supplies. Only a very small part of the total volume (only 1 or 2 liters out of about 600 to 700 liters per person per day) are used for drinking; nevertheless, the opportunity to use any of the water in the public system for this purpose is cherished. These standards have therefore been universally adopted in the U. S. for water as delivered to the consumer in public water supplies.

Table 1. Trace metal effects in water

Element	Toxicity	Color	Taste	Slime	Other
As	high				
Ba	high				
Cd	high				
Cr^{6+}	high				
Pb	high				
Se	high				
Ag	high				
Hg	high				
Cu	low		X		corrosion
Fe	low	red	X	X	
Mn	low	black	X	X	
Zn	low		X		irritant

Table 2. USPHS Drinking Water Standards

(U. S. Public Health Service, 1962)

Trace Element	Recommended limit (mg/l)	Mandatory limit (mg/l)
Pb		0.05
As	0.01	0.05
Ba		1.0
Cd		0.01
Cr		0.05
Cu	1.0	
Fe	0.3	
Mn	0.05	
Se		0.01
Ag		0.05
Zn	5	
Hg		0.005
Sr^{90}		10×10^{-9}
Ra^{226}		3×10^{-9}

The Public Health Service Drinking Water Standards were last revised in 1962 (Table 2). Maximum permissible concentrations or mandatory limits are provided for the toxic metals. Any public water supply which does not meet these standards will not be approved. In addition the standards provide recommended levels for those trace metals which create unaesthetic or other undesirable effects but which are not highly toxic. These include copper, iron, manganese and zinc. Public water supplies which do not meet these recommended limits will not be disapproved, but other supplies are recommended.

The mandatory standard for mercury has been tentatively established at 0.005 milligrams/liter by the Public Health Service. It is interesting to note that the illinois Pollution Control Board has adopted a mercury standard for water in streams and in effluents discharging to Illinois streams which is 1/10 the tentative drinking water standard. The drinking water standards do not set concentration limits in milligrams/liter for strontium-90 and radium-226. The limits have been established as 10 picocuries/liter for strontium-90 and 3 picocuries/liter for radium-226. The values for these isotopes as shown in Table 2 have been converted to concentrations in milligrams/liter on the assumption that 1 gram of radium is equivalent to 1 curie.

Standards for some other uses are shown in Table 3. The permissible standards for public water supplies for copper, lead, zinc, and iron are the U. S. Public Health Drinking Water Standards. The next line indicates the desirable level arbitrarily set by the American Water Works Association as an "ideal" water. Copper, zinc and iron should be virtually absent; lead should be absent. "Virtually absent" really means "below the detectable limit." "Absent" means "low enough not to have any effect."

General farmstead use generally follows the Drinking Water Standard because farm people do drink some water. Livestock likewise drink some water--note that lead has been specifically prescribed for livestock, however. The values for dairy sanitation are based more on the effects of iron in producing red water problems and bacterial slimes. Industrial waters are primarily related to iron again because of its problem with color, which would interfere with such things as textile and high quality paper processing. There is difficulty in producing white paper from red water.

Trace metals found in surface waters of the United States are shown in Table 4. The Federal Water Pollution Control Administration sampled and analyzed surface waters for many impurities. Kopp and Kroner (1967) summarized the results of 1,577 samples of surface water collected across the nation in the Federal Water Quality Administration surveillance program. The number of positive samples is the number of samples containing this element in concentration above the detectable limit for the analytical procedure used. Almost all samples had detectable amounts of strontium, most had detectable levels of iron and copper, much fewer had cadmium and arsenic. The range indicates that the frequency distri-

Table 3. Recommended permissible concentrations of heavy metals in water.

(National Technical Advisory Committee on Water Quality Criteria to Secretary of Interior, 1968)

	Recommended Limits (mg/l)			
	Copper	Lead	Zinc	Iron
Public Water Supply:				
Permissible	1.0	0.05	5	0.3
Desirable	v. abs.	abs.	v. abs.	v. abs.
Fresh Water Organisms: (fraction of 96-hr TLm)	1/10		1/100	
Agricultural use:				
General farmstead use	1.0	0.05	5	0.3
Livestock		0.05		0.1
Dairy Sanitation				0.1
Irrigation:				
continuous	0.2	5.0	5.0	
short term	5.0	20	10	
Industrial Use:				
Boiler makeup				80
Cooling water:				
fresh				14
brackish				1
Textile	0.5			0.3
Pulp and paper				2.6
Chemical				5
Petroleum				15
Food Canning				0.4

bution is highly skewed. Large numbers of samples would be expected to have low concentrations, and a few would have concentrations in the higher end of that range. The number of violations is the number of these surface water samples which had concentrations of the indicated element higher than the established limit shown in the last column. The limit, of course, is the Drinking Water Standards expressed in ppb instead of ppm; i.e., in micrograms per liter instead of milligrams per liter. Only 41 out of the 1,577 samples had arsenic in excess of the 50 microgram/liter standard, for example. Most surface waters do not contain trace elements in excess of established standards. The data for the mercury indicate some 39 samples were positive and only a few exceed the limit of 5 ppb. *(USGS, 1970)*.

Table 4. Trace element concentrations in surface waters.

(Kopp and Kroner, USGS Prof. Paper 713)

Element	No. Positions 15 μg samples	Frequency %	Range μg/l	Violations	Limit μg/l
As	87	5.5	5-336	41	50
Cd	40	2.5	1-120	6	10
C Cr	306	24.5	1-112	4	50
Cu	1173	74.4	1-200	0	1000
Fe	1192	75.6	1-4600	25	300
Pb	305	19.3	2-140	27	50
Mn	810	51.4	0.3-3230	74	50
Sr	1571	99.6	3-5000		
Hg	39	49.3	0.1-17.0	--	5

Trace elements in Illinois waters have been studied only slightly. There are two sets of Illinois waters of particular interest: Lake Michigan, because it furnished water for half the population in the state through the water systems of the City of Chicago; and the Illinois River System. The data in Table 5 are from two separate studies. The Lake Michigan data are from analyses made by the laboratory at the Water Department of the City of Chicago *(Vaughn, 1971)* and they indicate very low concentrations (ppb levels) of cadmium, copper, manganese and zinc. Levels of the other elements indicated below detectable limits in raw Lake Michigan water. This is only a very small sample, but the orders of magnitude are typical of the entire record. The Illinois River data

(Mathis and Cummings, 1971) show that water in the Illinois River has ppb levels of many of these elements. Note that in the case of chromium, cadmium and lead the levels are in the ppb or tenths of ppb range. In some small creeks that are tributaries to the Illinois River but which are affected neither by the Industrial activity on the Illinois River nor by the discharge of the Metropolitan Sanitary District of Greater Chicago, one finds substantially lower concentration of cadmium, chromium and lead. Zinc, however, is about the same.

Table 5. Trace elements in Illinois waters.

(μg/1)

Element	Illinois Creeks	Illinois River at Peoria	Lake Michigan at Chicago
As			ND
Cd	0.1	0.6	1-2
Cr	2.5	22	ND
Cu		1.1	1-2
Fe			ND
Pb	0.3	2.1	ND
Mn			4-15
Zn	23	29	4-16
Hg			< 0.1

Sources: Mathis and Cummings
Vaughn

The concentrations of these trace elements in surface waters of the state and of the nation are generally lower than the accepted standards. However, there are places where there are exceptions and where the concentration is high enough that some removal is needed.

In both the Illinois River and in Lake Michigan, bottom sediments have 10^3 or 10^4 higher concentrations of these trace elements than the water which overlie those sediments (Table 6). In the case of the Illinois River, the concentrations are in parts per billion in the water, and tens of parts per million in the sediment. The data on Lake Michigan sediments are taken from some recent data from the State Geological Survey (Shimp, *et al*, 1970). The water data are taken from the City of Chicago *(Vaughn, 1971)*. In general, the trace metals in the water will be low, but the trace metals in the sediments may be quite high. This is important to the biological forms which are particularly associated with the bottom sediment. Bottom feeding organisms (tubificid worms, for instance) often have very high concentrations of trace metals. It is also significant to us from the water treatment standpoint. When the stream is in flood stage and the heavy sediment load is in suspension, the water is highly turbid. Much trace metal will be associated with that suspended matter and is relatively easily removed by conventional water treatment processes.

Table 6. Trace elements in bottom sediments.

	ILLINOIS RIVER		LAKE MICHIGAN	
Element	Water µg/l	Sediments µg/kg	Water µg/l	Sediments µg/kg
As			ND	13,000
Cd	0.6	1,100	2	17,000
Cr	21	7,000	7.6	64,000
Co	2.8	3,400	4	10,000
Cu	1.2	16,000	2	109,000
Pb	2.6	28,000	< 4	90,000
Ni	2.9	12,000	< 1	35,000
V				54,000
Zn	2.9	73,000	5	179,000

Table 7 presents a summary survey of trace metal concentrations in the public water supplies distributed in the water distribution system for the 100 largest cities in the United States (*Durfor and Becker, 1964)*. The percent of those public water supplies which had less than the indicated concentration clearly indicates that almost all public water supplies have concentrations of less than accepted standards. The concentrations indicated are not in all cases the Public Health Service Drinking Water Standard. The indicated oncentration of lead is 10 micrograms/liter; the standard is 50 micrograms/liter. Since some of the data indicate the minimum is non-detectable, the median should be indicated as a "less than" value. The skewed nature of the distribution is reflected by comparison between the minimum, the median, and the maximum. Lead has a median value of 2.7 and a maximum value of 34. Maximum values in excess of Drinking Water Standards are noted, and it is that fraction which requires treatment for removal of excess heavy metals. A decontamination factor of about 10 is usually needed. This requires removal of about 90% of the concentration of the trace metal in that particular water supply to meet the standard.

Table 7: Trace elements in public water supplies of 100 largest U. S. cities.

(from USGS Water Supply Paper 1812)

Element	Concentration (μg/l)	% less than	Max.	Median	Min.
Ag	0.50	95	7	0.23	ND
Al	500	87	1500	54	3.3
B	100	94	590	31	2.5
Ba	100	94	380	43	1.7
Cr	5	95	35	0.43	ND
Cu	100	94	250	8.3	< 0.6
Fe	250	98	1700	43	1.9
Li	50	96	170	2	ND
Mn	100	97	1100	5	ND
Mo	10	96	68	1.4	ND
Ni	10	95	34	2.7	ND
Pb	10	95	62	3.7	ND
Rb	5	91	67	1.0	ND
Sr	500	96	1200	100	ND
Ti	5	96	40	1.5	ND
V	10	91	70	4.3	ND
U	Z	93	250	0.15	< 0.1

Conventional water treatment is intended for clarification, *i.e.*, for removal of suspended matter, silt, sediment and bacteria. Consequently, a conventional water treatment plant for a public water supply treating a surface water may use coagulation, sedimentation, filtration, and finally, disinfection. Coagulation is provided by the addition of aluminum sulfate, or in many cases iron salts such as ferrous sulfate or ferric chloride, followed by a rapid mix and then slow stirring to promote flocculation (the agglomeration of colloidal particles into macroscopic floc). That process is then followed by sedimentation, which removes the bulk of the suspended matter and the associated coagulant. The fine pin-point floc that settles too slowly to be effectively removed by sedimentation is then removed by filtration through a layer of some 30 inches approximately of either sand or crushed and graded anthracite coal or some mixture of these. The filtered water is typically chlorinated for disinfection. The treatment is highly effective for removal of suspended particles. Virtually all particles one micron in diameter or larger are removed. Consequently, that fraction of the trace metals associated with clays and with silt particles tends to be removed in this fashion.

Barnett, *et al.*, *(1969)* presented some data on the removal of trace elements from the Denver water supply (Table 8) where water is taken from high mountain lakes, water which is otherwise of very good quality and is treated by the conventional process just described.

Table 8. Trace element removal by conventional water treatment - Denver water supply.

(from Barnett, Skougstad and Miller, 1969)

	Concentration (μg/l)		
Element	Raw	Filtered	% Removal
Ba	18	20	none
B	12	11	8
Cr	ND	ND	--
Cu	120	20	84
	85	12	
	45	8	
	35	6	
	24	14	
	26	7	
	34	7	
	65	3	
Fe	46	5	90
	5	5	none
	39	8	
	40	6	
	23	30	none
Mo	48	40	16
	140	140	none
	60	51	15

The data (Table 8) shows no removal of the barium. Boron is 8% removed. Chromium was not detectable anyway. Copper is highly variable. Some days good removal was obtained, and other days removal was not so good. Analyses for total copper content do not delineate the fraction association with the suspended matter and therefore provide little information about the prospects of removing it by the conventional treatment. In environmental surveillance, we must make analyses that are more meaningful in terms of our objective. Similarly, removal of iron ranged from 90 percent to none. If iron is oxidized, it is removed pretty well; but if dissolved, it will not be removed very well by clarification processes. A trace metal which happens to be associated with silt, clay particles, bacteria, ought to be effectively removed by a conventional water treatment process.

The trace metals that have been studied most widely are iron and manganese. Much research is being devoted to these two metals because we have a far greater number of water supplies that have problems with them. There are a variety of ways of removing iron and manganese. They are both similar and are both removed by the same processes. The most typical process for a municipal plant is aeration, to oxidize the ferrous and manganous species and precipitate the metal. Aeration is followed by some sedimentation, but normally the removal of that fine precipitant is by filtration on a sand or anthracite filter. The process sometimes works and sometimes it is not effective. Research on iron removal was started at the University of Illinois about twelve years ago because Central Illinois has many ground waters that are high in iron concentrations. Iron concentrations of 5 milligrams per liter are not uncommon where the standard is about 0.3. Again we are looking for that decontamination factor of roughly 10,--a little more in this case. Research confirmed that aeration usually provides adequate oxidation of the iron. Failure to convert to the ferrous state was not the principle difficulty. (*Ghosh, et al., 1967*).

Further research investigated organic compounds in the ground water which complex the iron, but were found not to interfere with its removal (*Robinson, et al., 1967*). The removal of iron was found to be far better after the sand filter bed had been "ripening" for awhile. Ripening refers to the development of a deposit of iron and bacteria on the sand after running iron-bearing organic-laden, aerated water, through a sand filter for a period of weeks, and that promotes more effective removal. The further ripening of the filter, however, made the situation worse. After a longer period of ripening there tended to be a breakthrough of ferrous iron so that if iron removal had been obtained it was now lost again. It was speculated at first that accumulation of bacterial slime resulted in oxygen depletion in the sand bed and set up reducing conditions. This permitted the iron that had been removed to revert to the soluble ferrous state and leach out of the filter. However, further sudy indicated that it was not just bacterial slime growth. The oxygen depletion is related to the nitrifying organisms and ammonia content of the well waters. Even in a very conventional, very mundane water treatment process like aeration and filtration for removal of iron and manganese we find some complication factors.

Often ground waters and less often surface waters will have so much calcium and magnesium that they will be objectionable from the standpoint of hardness. Conventional process for removing that hardness is to precipitate excess calcium as calcium carbonate by addition of lime, calcium hydroxide. A conventional water treatment plant with coagulation, sedimentation, filtration, and disinfection is applicable if facilities for feeding lime are provided. The coagulation not only removes already suspended particles, but also the precipitated calcium carbonate. The sedimentation settles most of it out; the rest is removed on the sand filter as a physical separation process. The softening process is effective in the removal not only of calcium and magnesium, but also other divalent and trivalent metals. The lime phosphate softening process is very effective in removing trace elements.

If one is looking for a very high decontamination factor for trace concentrations, a mass action effect may give difficulty in obtaining the necessary decontamination with this sort of a precipitation process. Much of the research that has been done in this precipitation area for removal of trace elements was done in connection with radio nuclides. Much research has been directed toward the removal of strontium, for instance. Since a very low concentration of strontium occurs initially, and since the objective is a level of about 10^{-9} parts per million, the decontamination factor must be not 10, not 100, but many thousands, in fact, hundreds of thousands--perhaps a million. To obtain such a high decontamination factor, one must go to some other process.

Ion exchange will give you very high decontamination factors. This, however, is dependent upon the chemistry of the ion exchange process as well. An interesting example is the removal of a trace metal not from a public water supply but from an industrial waste. The University of California at Davis was conducting experiments on strontium diet in beagles. They had many dogs in kennels on a strontium diet. A waste treatment process for the laboratory and kennel waste was required. A conventional biological waste treatment process was used to decompose organic matter. The strontium still had to be removed. Because the waste contained such low concentrations and the treatment had to meet such high decontamination factors, there was danger that there would be a leakage or break-through of a small trace of strontium through the ion exchange column. For that reason, a series of four columns was used. Upon onset of any indication of a break-through of strontium in the first column, that column was removed and another clean column added to the end of the line. It is possible to get very high decontamination factors for trace metals if additional expense is justified.

There are some other techniques for removal of trace metals. Clay materials may be used for absorption or ion exchange of the trace metal. This is a different way of getting an ion exchange reaction; instead of percolating the water through a resin bed, the ion exchange reaction occurs in a slurry. The metal is then removed with the clay by sedimentation and filtration. Reimer and Toth (1970) studied a number of clays and organic materials such as the humic acid (Table 9).

Table 9. Cation-exchange removal of copper.

Reimer and Toth (1970)

Material	CEC (me/μ/g)	Cu(10 ppm) Adsorbed	Cu(2.5 ppm) Adsorbed
Kaolinite	5.4	5.0	2.5
Illite	33.4	7.4	2.5
Montmorillonite	69.8	9.6	2.5
Humic acids	250.9	9.2	2.5

The cation exchange capacity of kaolinite is low (about 5 milliequivalents per 100 grams) but not insignificant. When they added 10 parts per million of copper, virtually all of it was adsorbed on the clay. Illite has a higher exchange capacity; removal is better. Montmorillonite is even better than illite. Humic acid is similar to montmorillonite. These exchange materials can be used to remove trace metals. A very successful example is the treatment of radioactive waste at Oak Ridge National Laboratory where lime phosphate softening is used for removing the trivalent cations and the strontium and radium. Cesium was not being removed very well in that process, however, so illite clay is added to their waste before the lime phosphate process. The lime phosphate sludge carries down with it the added illite and the cesium associated on the cation exchange sites.

Another technique is the use of foam separation methods. Table 10 shows six different conditions under which we can remove suspended and dissolved materials by adding a foaming agent and then bubbling air through a column of water *(Rubin, 1968)*.

Table 10. Foam separation.

Flow rate	Molecular	Microscopic	Macroscopic
High	Foam fractionation	Foam flotation	Froth flotation
Low	Ion flotation	Micro-flotation	Precipitate flotation

In the case of macroscopic particles, if one uses a high airflow rate, and adds surface-active frothing agents, one can float suspended particles and separate them from the water. The technique has been highly developed in the mineral-refining industry. It is a long established procedure for refining metal ores. One can do the same thing with molecular impurities if one adds a surface-active agent which will complex the metal and then use a high flow-rate. The surface-active agent concentrates at the air-water interface of the bubbles and in doing so it also concentrates the complexed metal. The foaming separates the metal-organic complex from the water and the foam is skimmed off the top. Recently some other techniques have been developed using lower air flow-rates. In the case of the molecular impurities or ionic species, this is called "ion flotation." If the metals are associated with micro-organisms and then floated, the process is called "microflotation". If precipitated floc is being floated, the process is called "precipitate flotation". Table 11 presents some results reported by Rubin (1968).

Table 11. Sodium lauryl sulfate flotation.

Rubin (1968)

Fe	0.2 mM	Precipitate ion	98% in 15 min. 35% in 30 min.
Cu	0.3 mM		95% in 3 min.
Pb	0.1 mM		75% in 2 hours

Sodium lauryl sulfate was used as the flotation agent. If iron at 0.2 millimolar concentrations is oxidized previously so that it is precipitated, 98% removal of that iron was obtained in 15 minutes of aeration. If it is not precipitated so it still exists as the ferrous ion, then only 35% removal resulted in 30 minutes aeration. For copper, good removals were observed, but lead did not respond as well.

There are techniques involving membrane processes, such as electrodialysis or reverse osmosis. These provide very high removal of almost any kind of impurity. Distillation offers decontamination factors for virtually any kind of nonvolatile impurity of the order of 10^6 --very high decontamination factors.

Generally, since we seldom are faced with a water treatment problem that is primarily removal of trace elements, but usually a secondary consideration in a treatment operation, we normally do not find that the trace element is much of a problem. Consequently, we have had little study on it. Where we do find concentrations in excess of the recommended standards, they normally are only on the order of a magnitude higher and a decontamination factor of 10 is adequate. For that reason, techniques such as aeration, coagulation, filtration, softening, chemical precipitation techniques, and ion exchange method, are usually adequate. If we had to use something better, there are methods such as the clay exchange, adsorption on activated carbon, and foam separation. With the exception of radioactive waste, we do not need such expensive and such sophisticated techniques as electrodialysis and reverse osmosis, or distillation.

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WATER QUALITY AND EFFLUENT STANDARDS FOR TRACE METALS

S. R. Aldrich

The Illinois Pollution Control Board (hereafter referred to as the Board), established by the Environmental Protection Act of 1970, is in the process of conducting hearings on proposed standards as a basis for establishing water quality and effluent standards that will protect and/or improve Illinois streams and lakes. It is a difficult and exacting task, but one that is of crucial importance to the future of surface waters in Illinois. It may, in addition, serve as a model for many other states.

Though the Board is aware of the introduction of certain trace elements (mercury, cadmium, etc.) into the atomosphere, it has no pending programs for emission control.

Establishing the proper standards and effectively explaining them to the many and diverse interest groups so that they are accepted as being in the total public interest will be a major factor in determining the credibility of the Pollution Control Board. It should not be inferred from the preceding statement that the Board is engaged in a popularity contest. It will be impossible for the Board to set standards that are completely acceptable to such diverse special interests as conservation groups at one end of the spectrum and affected industry at the other end.

The Board must consider protection of human health, the preservation of the environment for the biota and for esthetic qualities, and the conservation of natural resources of trace elements. The Board must strive to strike theproper balance between those considerations and both long term and short term economic impact. One of the recently acquired dimensions to environmental issues is that some short-term benefits must be sacrificed in favor of long-term gains. It is currently popular in some quarters to blame previous generations for greed and thoughtlessness in the use and abuse of the environment. In my opinion that view is unfair, false and either non-productive or even counter-productive. I believe that environmental protection and improvement should be a crusade rather than a vendetta.

I. BASES FOR STANDARDS

A. Toxic levels for man - specific health effects: In spite of the view held by some persons, I feel that man has a special place on the earth and that his health and well-being are first-order considerations. Insofar as possible, we must recognize that the threshold tolerance of a small percentage of the population is well below that of the majority because of special sensitivity (analagous to allergic sensitivity).

The recent trend is to build an ever larger safety factor into the standards. This is entirely a matter of judgement and one's particular point of view. It is inextricably tied to both technical feasibility and economic reasonableness, which are discussed in the following sections.

B. Discomfort levels: Standards for certain parameters are likely to be set at levels which some persons find objectionable even though below a health hazard. Phenols, for example, are detectable and objectionable at a level well below the health hazard.

C. Potential for concentration within the biological chain: Some elements are capable of being concentrated to the dangerous level within the biological chain. Mercury is, for example, reported to have been concentrated 3000 times from the level found in water to that found in northern pike fish. In such cases the water quality standard must take into account the potential for concentration, rather than only the direct toxic level for human drinking purposes.

D. "Technical feasibility and economic reasonableness": The Illinois Environmental Protection Act requires the Pollution Control Board to consider "technical feasibility". This is a rather straightforward determination dependent upon the availability of control or removal technology. The Act further stipulates consideration of "economic reasonableness." This obviously is subject to a wide range of interpretations.

A basic guiding principle is that the costs of control or removal of any pollutant is on *an increasing curvilinear* rather than a linear line. It likely is fairly accurate to assume that the last *10* percent of control will cost as much as the first *90* percent, and the last *1* percent as much as the first *99* percent. Hence, the decision must be made at some point on the curve, that the added benefits do not justify the costs of more complete pullution abatement.

A point often overlooked by special interest groups is that the Board is considering pollution abatement programs that will have impact at hundreds of points in the economy. Each discrete decision cannot be made in an economic vacuum. The Board has said that it will not sanction the piecemeal destruction of Lake Michigan by small thermal inputs, each insignificant (except locally) but eventually contributing to an aggregate that will markedly accelerate the aging of the lake. Similarly, the aggregate costs to the public of many pollution abatement measures resulting from water quality and effluent standards must be considered by the Board.

Assuming that the public wants to achieve the greatest overall environmental improvement for added costs (in terms of costs for all goods), the Board is challenged to determine the proper level of control for each parameter.

Recovery and reuse of many elements or compounds will partially offset the cost of removal, thus reducing the economic impact of requiring removal in order to protect the environment. Another way in which pollution abatement partially pays for itself is in the form of reduced costs for pretreatment of water by downstream industries and municipalities.

In order to establish priorities for action by the Board, I suggest two classes of problems: First are those that are *accute, irreversible,* and that *affect health or survival* (mercury is an example). Second are those that are *chronic but low level, reversible,* and that *affect esthetic values* (thermal inputs are an example).

II. PROCEDURES FOR SETTING STANDARDS

Step 1. A proposed (tentative) standard or regulation

Proposals may be generated by members of the Pollution Control Board (e.g. state water quality standards), the Environmental Protection Agency (e.g. regulations on animal wastes), the Institute for Environmental Quality, or by a citizens' petition bearing at least 200 signatures (e.g. noise standards for O'Hare Airport).

The proposed standard is distributed for public review.

Step 2. Public Hearings

Public hearings are held for the purpose of developing a record that provides an adequate basis for decisions by the Board. The Act requires two hearings at different locations for standards that affect the entire state. In the case of effluent standards, the Board scheduled eight hearings. Approximately ten will be held on the application of plant nutrients.

A diligent effort is made to schedule witnesses from the scientific community (representing more than one viewpoint where appropriate), from affected industries or individuals, and from interested citizens. A complete and well-balanced record is the goal. Testimony is solicited from Agency personnel. The Institute often assists in obtaining expert witnesses by supplying travel expenses.

The record is usually kept open for one to several weeks after the last scheduled hearing, during which additional information will be received. If significant new information or problems are brought to the attention of the Board, additional hearings will be scheduled. This was done in the case of mercury at the request of paint manufacturers who did not testify in the first set of hearings.

Step 3. Final public review

The Board develops the proposal in final form and distributes it for public review.

Step 4. Adoption, preparation and publication of an opinion

The Board formally adopts the proposal upon an affirmative vote of at least three members (there are five Pollution Control Board members).

One member of the Board is requested to prepare an opinion summarizing the hearing record and explaining the basis for the opinion.

Not more than two Board members may dissent from the majority opinion. Dissenters write a separate opinion(s) which accompanies the majority opinion. Individual Board members often disagree with certain sections of the majority opinion and write supplemental statements expressing their viewpoint.

Board members consider the preparation of opinions to be one of their most important responsibilities. Opinions are concise, informative, factual summaries of testimony accumulated from one to several days of hearings, plus literature entered as exhibits into the hearing record. The opinions should become major reference sources for agencies or individuals who are interested in environmental affairs.

III. PROPOSED WATER QUALITY STANDARDS

The Illinois Pollution Control Board has developed proposed water quality standards and distributed them for hearing purposes. The proposed standards are goals for both surface and ground waters in Illinois. All waters are expected to meet minimum general standards except for certain restricted-use waters (see below). Several water use designations are established:

1. Primary contact (swimming, water skiing). Waters expected to meet fecal coliform standards more restrictive than the general standards during the recreational season.

2. Public and food-processing water supply. Waters expected to meet the U. S. Public Health Service Drinking Water Standards of 1962 with only conventional treatment processes. Also expected to meet criteria more restrictive than the general criteria for a number of chemical constituents. Underground waters are expected to meet these more restrictive standards as well.

3. Restricted use waters. Certain low-quality waters not expected to meet general standards for certain parameters.

4. High quality waters. Waters designated for special protection. Expected to meet standards higher than the general standards for dissolved oxygen and fecal coliforms.

5. Lake Michigan waters. Expected to meet certain more restrictive standards in addition to the general criteria and public and food processing water supply criteria.

IV. "NO DILUTION" CONCEPT

The Board has tentatively decided than an industrial plant may not add water to dilute its waste water from processes within the plant in order to meet effluent standards at the point of discharge to a stream or lake.

This poses a special problem when the intake water is already at the water quality standard for the receiving water. An industry in that predicament would need to remove 100 percent of the element introduced by its manufacturing process. The problem is that the cost to remove the last 1% may be as great as to remove the first 99%. In practice, the no-dilution concept may force completely closed systems or closure of the plant. The Board has yet to decide whether natural downstream dilution may be recognized in setting the standard for discharges into surface waters. The no-dilution approach has a sound rationale in that it is more feasible to use highly sophisticated removal technology on a small volume of effluent than on a large one. Thus, non-dilution promote, the concept of complete, or nearly complete, recovery of elements for productive use, rather than treating them as wastes.

V. NON-DEGRADATION POLICY

The Illinois Pollution Control Board is moving in the direction of a policy which states that streams which are now purer than state-wide minimum standards may not be degraded. When combined with the no-dilution concept previously discussed, the non-degradation policy prevents industries from moving from sites on streams that are already at the upper limit of certain pollutants to less loaded streams in order to avoid having to remove 100% of certain pollutants.

VI. PRECISION OF DETERMINATIONS

Problems associated with valid determinations are easily overlooked or underestimated.

A. Sampling: Certain emissions are difficult to sample because of their location, i.e. from a 500-foot smokestack. Some emissions are highly variable over short intervals of time, i.e. smoke emissions from various types of combustion chambers. A good example of this occurred in connection with sampling smoke from the Springfield power generating plant in the spring of 1971. Results from the sample extrapolated to a year indicated a discharge of 5300 pounds of mercury per year. But the coal consumed annually contained only 115 pounds. Obviously the rate of mercury discharge at the time of sampling was atypical.

B. Analytical: Some of the parameters of concern are at such extremely low levels (i.e. .5 ppb mercury) that analytical procedures are severely taxed. Furtheremore, many newly-established laboratories or poorly-qualified technicians are making determinations.

A researcher in Chicago sampled public water supplies and analyzed for mercury. He held a press conference and announced that some drinking water sources contained up to 18 ppb (36 times the Illinois effluent standard). The water quality laboratory for Chicago later reported that the analytical procedure was in error and that no dangerous levels of mercury were present in the public water supplies that were tested.

Another researcher, dealing with measurements on water from Lake Michigan, stated that "...results are very disheartening because on the same sample there was as much as a 20-fold difference in results" (Dr. Donald I. Mount, Progress Report on Lake Michigan Interstate Pesticide Committee, Multilithed. March 23, 1971). Dr. Mount further commented that of "six key laboratories reporting, three were consistently finding values about five times higher than the other three." Tissue analyses of fish were much less variable, with an "interlab variation of only two to three times" among eight laboratories.

C. Problems for the Pollution Control Board and the Environmental Protection Agency:

The Board must consider the feasibility of reliable measurements in selecting standards. Otherwise, the Agency will not be able to successfully prosecute cases before the Board.

The Agency must have available to it, accurate and reliable measurements, not only to make its case against an alleged violator, but also in fairness to the alleged polluter.